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THE CAUSES AND
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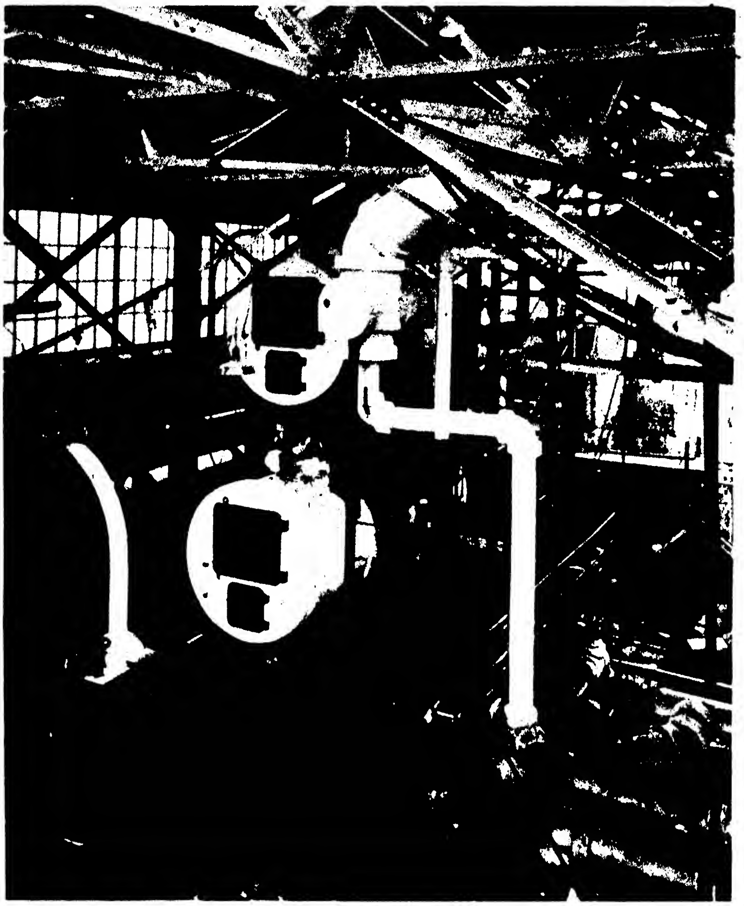

[*Frontispiece.*

AN ELLIOTT DEGASSER. 250,000 POUND UNIT.

THE CAUSES AND PREVENTION OF CORROSION

BY

ALAN A. POLLITT, M.Sc. (Tech.)

Associate of the Manchester College of Technology
Member of the Institute of Metals

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PREFACE

Whilst the subject of corrosion is by no means unrepresented in technical literature, particularly that published during recent years, much of it is, unfortunately, scattered, and there does not appear to exist any work which deals in a comprehensive manner with the practical aspect of the problem, its causes, and the methods available for protecting our metals from it.

In preparing this text-book it has been the author's endeavour to present, therefore, as completely and concisely as possible, the more interesting and practically useful information on the various phases of this subject, and although, because of the incompleteness of our knowledge in many directions, the work cannot claim to be thoroughly complete, yet it is hoped that it will provide a convenient reference book to all whose activities bring them into contact, and conflict, with corrosion problems and to whom much of the original literature may often be difficult and inconvenient to obtain and survey.

A theoretical treatment of the subject is necessarily included, since knowledge of this is essential to the successful diagnosis and prevention or alleviation of corrosion troubles. It has been dealt with, however, as briefly as is compatible with the object in view.

For generous assistance in providing illustrations and text matter the author wishes to acknowledge the following:

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Alan A. Pollitt.

June, 1923.

CONTENTS

PART I

THE THEORY OF CORROSION

CHAP. PAGE

I. INTRODUCTORY 13

The Susceptibility of Iron and Steel to Corrosion—Conservation of Resources—Recent Accumulation of Knowledge—Necessity for Research—Definition of the Term " Corrosion "—Its Misapplication—Corrosion an Ionic or Electrochemical Phenomenon—Modern Conception of Corrosion—Mutual Agreement between the two Principal Theories—Hydrogen Ions Essential to Corrosion—Practical Value of the Electro-chemical Theory—Reputed Resistivity of Olden Day Products—The many Phases of the Corrosion Problem.

II. THE THEORY OF CORROSION 19

Facts which a Tenable Theory must Explain—Solution and Osmotic Pressure—Electrolytic Dissociation—Modes of Ion Formation—Electrolysis—Polarisation—Oxidation—Hydrolysis—The Acid and Electrolytic Theories of Corrosion—Compatibility of these Theories—Mechanism of Corrosion—The Action of Carbonic Acid on Iron—Colloids and their Properties—The Colloid Theory of Corrosion—Its Substantiation—The Peroxide and Older Theories of Corrosion.

III. FORMS OF CORROSION 34

Auto-corrosion—Contact Corrosion—Externally Induced Corrosion—Effect of Stray Currents—Corrosion of Buried Iron—Auto-corrosion and Heterogeneity—Contact between Dissimilar Metals—Auto-electrolysis—Galvanic Protection of Metals—Galvanic Action—Heterogeneity—Pitting—Electrochemical Series of the Metals—Physical Heterogeneity—Ferroxyl—Passivity—Production and Properties of Passive Iron—Theories of Passivity—Destruction of Passivity.

PART II

THE CAUSES OF CORROSION

IV. THE FUNCTION OF OXYGEN 44

Factors Influencing Corrosion—Their Classification—The Action of Air and Water on Iron—Liquid Water Essential to Corrosion—Oxygen the Prime Factor in Corrosion—Action of Steam on Iron—Influence of Secondary Factors which Affect the Supply of Oxygen—Corrosivity of Soils—Corrosivity of Aërated Water—Rate of Flow of Water—Depth of Immersion of the Metal—Area of the Exposed Surface of the Water—Effect of Temperature—The Production and Behaviour of Rust—Its Composition—Rust Stimulative—Pitting—Formation of Rust Cones—The Influence of Oils on Corrosion.

CHAP. PAGE

V. THE INFLUENCE OF THE ELECTROLYTE ON CORROSION OF IRON . . . 57

Acid, Alkaline and Saline Media—Acid Salts—Acids Stimulative—Alkalies Inhibitive—Action of Nitric, Hydrochloric, Sulphuric, Phosphoric, Carbonic and Chromic Acids—Inhibitive Effect of Chromic Acid and its Salts—Inhibitive Effect of Alkaline Media—Stimulative Action of Low Concentration of Alkali—Critical and Limiting Concentrations—Recent Explanation thereof—Effect of Dissolved Salts of Greatest Importance in Connection with Boiler-feed Water.

VI. THE INFLUENCE ON CORROSION OF FACTORS INHERENT IN THE METAL . . 63

Difficulty in Determining Relative Corrodibilities—Choice of Material for Specific Purposes—Factors Inherent in the Metal and Influencing Corrosion—Their Classification—Effect of Variations in the Composition of the Metal—The Influence of Carbon, Silicon, Sulphur, Phosphorus, Manganese, Arsenic, Aluminium, Chromium, Cobalt, Copper, Nickel, Selenium, Silver, Tin, Lead, Tungsten, and Vanadium on the Rates of Corrosion of Metals containing them—The Influence of Surface Impurities—Mill Scale—Cinder and Slag Inclusions—Structural Heterogeneity—Segregation—Heterogeneity of the Electrolyte—Concentration Cells—Effect of Polishing on Corrosion—Physical Heterogeneity—Internal Strains—Ferroxyl—Effects of Cold-working—Surface Wounds—Summary of Stimulative and Inhibitive Factors—Note on the Corrosion of "Busy" Iron.

VII. WATER: ITS SOURCES, CHARACTERISTICS, AND IMPURITIES 78

Characteristics Determined by Impurities—Waters for Steam-raising Purposes—Corrosive Impurities—Scale-forming Impurities—Acquirement of Impurities—Classification of Natural Waters—Rain Water—Surface Drainage—Shallow Well Water—Upland Surface Waters—River Water—Self-purification of River Water—Spring and Deep Well Water—Hard and Soft Water—Hardness—Zeolites—Colliery Waters—Peaty Waters.

VIII. THE BEHAVIOUR OF IMPURITIES IN WATERS USED FOR STEAM-RAISING 86

Types of Boiler Troubles—Heat Losess Due to Scale—Classification of Water Impurities—Scale, Sludge and Scum-forming and Corrosive Impurities—Behaviour of Impurities under Boiler Conditions—Economiser Troubles—Scale and Corrosion—External Surface Corrosion—Boiler Troubles—Priming, Foaming and Bumping—Troubles due to Oil and Grease—Boiler Scale and Corrosion—Types of Scales—Behaviour of Corrosive Impurities in Feed-water—Chlorides and Nitrates of Lime and Magnesia—Iron and Aluminium Salts—Behaviour of Sodium Carbonate—Superheater Troubles—Corrosion and Choking of—Turbine Troubles—Corrosion and Accumulation of Deposits—Disposition of Corrosion in Turbines—Standing and Running Corrosion.

IX. THE CORROSION OF CONDENSER TUBES 107

Types of Corrosion—Uniform and Preferential Corrosion—Factors Influencing Corrosion—Oxygen Essential—Effect of Temperature—Effect of Saline Concentration—Action of Corrosion Products—Effect of Composition and Structure—Causes of Tube Failure—Laminations and Spills—Faulty Composition—Crystalline Structure—Mechanical Failure—Splitting—

CHAP. PAGE

Season Cracking—Accumulation of Corrosion Products—Settlement of Foreign Bodies in Tubes—Subsidiary Steam Supplies—Inlet Deterioration—Electrical Leaks—Water Speed—Froths and Foams—Design of Water-end—Ferrule Troubles—Presence of Iron Compounds—Short-circuiting of Contaminated Cooling Water—Variations in Water Composition—Complete and Selective Corrosion—Protection of Tubes—Electrolytic Methods—Tube Cleaning, Mechanical and Chemical—Oxidising Annealing—Protection by Insoluble Salts and Metallic Layers—Types of Water—Memoranda.

PART III

THE PREVENTION OF CORROSION

X. THE CONTROL OF IMPURITIES AND MANUFACTURE 132

Limitations of Protective Measures—Exclusion of Corrosive Influences—Elimination of Corrosive Influences—Classification of Protective Measures—Care in Manufacture of Material—Control of Impurities—Homogeneity—Unprotected Material—Increased Severity of Modern Conditions of Service—Design of Structural Material—Simplicity in Design to Facilitate Inspection and Repainting and to Reduce Risks of Dangerous Localised Corrosion—Contact between Dissimilar Metals—Choice of most Suitable Material for Specific Service Conditions.

XI. OXIDE AND NON-METALLIC PROTECTIVE COATINGS 136

Oxide Coatings—Bower-Barff Process—Electro-negative Character of Magnetic Oxide—Potential Stimulative Influence of Electro-negative Coatings—Limitations of Electro-positive Coatings—The Well's process—The Gesner Process—The Dewees-Wood Process—The Bradley and Bontempi Processes—The Ruffington Process—Electrolytic Production of Oxide Coatings—Heat-blueing—Summary of Oxide Coatings—The Coslett Process—Advantages and Application of—The Parker Process.

XII. METALLIC PROTECTIVE COATINGS 143

Types of Metallic Coatings—Relative Merits of Electro-positive and Electro-negative Metallic Coatings—Protective Coatings of Zinc—Methods of Application—Hot-Dip Galvanising—Sherardising—Electrolytic Deposition—Spraying—Nature and Theory of the Sherardising Process—Effect of Iron Content in Sherardised Coatings—Protective Coatings of Tin, Copper, Nickel and Lead—Lohmannising—Protective Coatings of Aluminium—The Calorising Process—Protection of Metals against High Temperature Oxidation—Nature and Application of Calorising—Applicability to Metals other than Ferrous.

XIII. PAINTS AND ALLIED COATINGS 156

Function of Paints—Sphere of Application—Essential Properties—Character of the Pigment—Composition and Preparation of Paints—General Desirable Properties—Impermeability—Elasticity—Excluding Property—Opacity—Spreading Quality—Paint Materials—Linseed Oil—Lead and Manganese Driers—Japan Driers—China Wood and Soya Bean and Poppy Seed Oils—Adulterants for Linseed Oil—Rosin and Rosin Oils—Turpentine—Pigments—Inhibitive and Stimulative—Classification of Pigments—Significance of Electrical Properties—Conductors—Insulators—Water-shedding

CHAP. PAGE

Properties—Addition of Gums—The Choice and Application of Paints—*Priming Coats*—Preparation of Surface Prior to Painting—Paints for Particular Purposes—Galvanised Iron—Tinned Iron—Marine Structures—Tunnel and Mine Work—Asphaltic Preparations—Japans and Bituminous Paints—Baking Japans—The Angus Smith Process—Processes for Providing Bituminous and Like Coatings—Limitations of Bituminous Coatings—*Sphere of Usefulness*—Summary of Various Pigments.

XIV. FEED-WATER TREATMENT 172

Seriousness of Troubles Due to Feed-water Composition Synchronising with Developments in Steam-raising Plants—Treatments Applicable to Feed-water—Softening Processes—The Chemistry of—Removal of Temporary and Permanent Hardness—Removal of Sodium Carbonate—Removal of Iron and Aluminium Salts—Calculation of Quantities—Boiler Compounds—Softening plants, Desiderata and Operation of—Hot Process Softeners—Continuous Blow-down—Permutit Softening—The Removal of Grease—Coagulation—Combined Softeners and De-Oilers—The Removal of Dissolved Gases—Chemical Degassing—Physical Degassing—Types of Plant for—"Closed Systems."—Electrolytic Methods of Preventing Corrosion—Summary of Behaviour and Removal of Impurities in Waters.

INDEX 223

LIST OF ILLUSTRATIONS

FIG. PAGE

An Elliott Degasser. 250,000 pound unit . . *Frontispiece*

1. The Many Phases of the Corrosion Problem 17
2. Graphic Representation of the Electrolytic Theory of Corrosion . 26
3. Graphic Representation of the Acid Theory of Corrosion . . . 26
4. Showing the Influence of Water-Speed on the Rate of Corrosion . 30
5. Steel Needles Mounted in Ferroxyl . 51
6. Steel Nail and Needles Mounted in Ferroxyl 52
7. The Formation of Rust Cones and Pits 53
8. Showing the Influence of Saline Concentration on the Rate of Corrosion 60
9. Showing the Influence of Saline Concentration on the Solubility of Oxygen and on the Rate of Corrosion 60
10. Stressed Iron Wire Mounted in Ferroxyl 73
11. Stressed Iron Wire Mounted in Ferroxyl 74
12. Stressed Iron Wire Mounted in Ferroxyl 75
13. Heavy Carbonate Scale from Economiser Tube 88
14. Section through Calorised Material . 152
15. Annealing Boxes showing Protection afforded by Calorising . . 153
16. Calorised and Uncalorised Pipe Unions 154
17. Kennicott Cylindrical Type Softener. 181
18. Kennicott Apportioning Gear . . 182
19. Paterson Cylindrical Type Softener . 183
20. Paterson "Osilameter" Measuring Bucket 184
21. Paterson "Osilameter" and Chemical Tank 185
22. Complete Paterson Apportioning Gear with Water Wheel as Fitted to Larger Units 185
23. Lassen-Hjort Cylindrical Type Softener 187
24. Lassen-Hjort Measuring and Mixing Gear 188
25. Lassen-Hjort "Positive Discharge Valve" 189
26. Lassen-Hjort Horizontal Type Softener 190
27. Paterson Horizontal Type Softener 191
28. Kestner Softener as Used in Conjunction with the Kestner Continuous Blow-down System . 193
29. Permutit Softening Plant . . 195
30. Lassen-Hjort Combined Softener and De-Oiler 197
31. Paterson Combined Softener and De-Oiler 199
32. Solubility of CO_2 in Water . . 201
33. Solubility of Oxygen in Water . 202
34. Sectional View of the Kestner Chemical Degasser . . . 203
35. General Appearance of the Kestner Chemical Degasser . . . 204
36. Weir Direct Contact Heater . . 206
37. Usual Arrangement of an "Open-Feed" System . . . 207
38. Conversion of an "Open-Feed" System to a "Closed-Feed" System and Installation of a Weir Direct Contact Heater . 209
39. Arrangement of the Weir "Closed-Feed" System 210
40. Elliott Physical Degasser. Vertical Type 212
41. Elliott Physical Degasser. Horizontal Type 213
42. Elliott Horizontal Degasser, Large Unit 214
43. Elliott de-Aëration System Applied to Hot Water Service Lines . 215
44. Application of the Cumberland Electrolytic Protection to a Surface Condenser . . . 216
45. Application of the Cumberland Electrolytic Protection to a Yarrow Boiler 217
46. Application of the Cumberland Electrolytic Protection to Economiser Tubes 217

THE CAUSES AND PREVENTION OF CORROSION

PART I

THE THEORY OF CORROSION

CHAPTER I

INTRODUCTORY

THE fact that our most useful material of construction is the one which is the most susceptible to the destructive action of natural forces, is one which calls for philosophical contemplation. No one will deny that the rapid decay of iron and steel is one of the most annoying and expensive matters with which the consumer has to deal. Chosen universally for their excellent mechanical properties, yet they are much less permanent than wood or stone or even other metals whose mechanical deficiencies render them unsuitable for general use. Lead and copper, for instance, when exposed to the atmosphere, usually become coated with a film of oxide, or other insoluble compound, which acts as a protection to the metal beneath. Under similar conditions iron and steel become covered with a loose hygroscopic layer of oxide which actually accelerates the further corrosion of the metal.

It is, in consequence, somewhat surprising that the subject of corrosion has been one of the neglected problems of engineering. Whilst the attention of countless investigators has been directed to the study of the physical properties and micro-structure of iron and iron alloys, yet the study of their decay was left for many years to a small minority who had the foresight to appreciate the growing importance of the problem and the initiative and ingenuity to attempt its investigation.

Recent years have evidenced, however, a growing tendency to pay greater attention to the conservation and economic use of our natural resources, and as a result the subject of corrosion has exercised the minds of engineers and other consumers to an increasing extent. Yet it is comparatively recently only that a sound fundamental knowledge of the process of corrosion has been reached. Controversies were rampant for many years, and even to-day supporters may be found for theories which are either entirely discarded or considerably modified. Chemists, physicists and engineers have each, in turn, studied those phases of the problem into contact with which their personal experience has brought them. Each has studied from a different point of view and each with a different mentality, and the result is now evident in the diversity of opinion still prevalent on even the most basic of principles and the widely diffused and often sparse nature of such information as is available. A brief survey of this literature is sufficient to reveal the conflicting character of many of the results and conclusions of different workers, excellent though their individual researches may be. It will also show that there are many aspects of the problem of corrosion which are imperfectly understood, and that it is frequently impossible to attribute a specific case of corrosion to any definitely established cause.

Although our knowledge is, therefore, still incomplete and contains many gaps, we are considerably better informed than was the case fifteen or twenty years ago, and the growing appreciation of the corrosion problem and its prevention has given a decided impetus to investigation work in this connection. A general agreement of opinion has now been reached on the mechanism of the corrosion of iron, and the influence of many factors, both external and inherent in the metal, is known and can, in many cases, be removed or counteracted. More resistant metals have been produced and methods of protection have been evolved, put into practice, and improved upon.

Any process which will prolong the life of our existing stocks of iron and steel will confer great service on civilisation in two ways, firstly in the direction just quoted, and secondly in helping to conserve an even more precious natural resource, namely, our coal. Civilisation could progress even were the available supplies of iron enormously reduced, but it is a matter of much speculation as to how we should carry on if deprived of coal. It may be pointed out that from four to five tons of coal, or its equivalent, are required to produce one ton of steel, which will revert to its original and more stable form of oxide in an incredibly short period if steps are not taken to preserve it.

The term " Corrosion " is one which is often applied to all forms which the decay or deterioration of metals may take, excluding, of course, mechanical failure. It has been used even in cases where damage has been the result of purely mechanical erosion, and it is commonly used where oxidation has been directly produced by exposure to high temperatures, either in air or in superheated steam. It is not an easy term to define, but for our purpose it may be considered as including all cases of decay in which moisture is present and plays an active part, and which would not occur in the absence of moisture. In order to avoid confusion, it would seem desirable to impose some limit of this kind; and, therefore, the oxidation of metal due to heat alone, such as in furnaces and metal generally whose service involves contact with abnormally hot atmospheres, and the oxidation of the blades on the superheat stages of a turbine, will not be regarded as corrosion. We may therefore define the term as follows :—

> " Corrosion is a surface phenomenon and consists primarily and essentially of a solution of the metal; or, in the case of an alloy, of one or more of its constituents; through contact with an electrolyte."

This definition, though somewhat comprehensive, is a rigid one. An electrolyte is always essential though the contact between it and the metal may be either continuous or intermittent, and the electrolyte may be a poor conductor like pure water, or an excellent one such as a concentrated saline solution. Nor must it be taken that corrosion can proceed in all electrolytes nor that all metals will corrode in one particular electrolyte. In many cases the concentration of the electrolyte has an important influence. Frequently, also, some other factor must be present in addition to the liquid conductor before corrosion can proceed, but these factors, in the absence of an electrolyte, will not initiate corrosion. It may be anticipated, therefore, that corrosion is an electro-chemical or ionic phenomenon. This definition is applicable also to the decay of many non-metallic materials. The weathering of rocks, for instance, is generally the result of the corrosion or solution of some constituent by an electrolyte and may or may not be accompanied by erosive influences. The decay or rotting of wood is also accomplished in an analogous manner.

Friend (*The Corrosion of Iron*, Carnegie Scholarship Memoirs, Vol. XI., 1922) observes two types of the corrosion of iron which he designates "Surrosion" and "Erosion." The first term he applies to those cases in which the metal corrodes in a neutral medium, resulting in the production of an insoluble oxide which adheres to the underlying metal and which is commonly known as rust.

The second term, erosion, he reserves for cases of corrosion in which the products are more or less soluble salts and where the metal surface is left exposed to further attack. Such a distinction is of course useful from an academic point of view, but as the term "erosion" is generally understood to imply a mechanical action, comparable to a sand-blast, it will not, in order to avoid confusion, be used in this book in any other sense. Corrosion will be used in connection with all processes which may be included in the definition given above, the different types of corrosion being distinguished in other ways.

Two theories, the Acid theory and the Electrolytic theory, hitherto distinct and opposed, are combined and brought into agreement by the present-day conception of the mechanism of corrosion. Though each still retains to an appreciable extent its quota of adherents, yet an impartial consideration of each from the obviously common ground of the theory of solutions will lead to the conviction, now shared by the majority of the leading authorities, that they are mutually in agreement, and that whilst an academic distinction may be drawn between them, yet is there no essential practical difference. It is chiefly through the failure to regard the electrolytic theory broadmindedly, and its wider application as concerning ionisation, that the controversy between its supporters and those of the Acid theory has been so prolonged. Both theories may be equally well interpreted electrolytically. It will be shown that the presence of hydrogen ions is necessary to initiate the corrosion of pure iron in pure water. Both the Acid and the Electrolytic theories demand the acceptance of this, but whereas the former supplies these ions by stipulating the presence of an acid (which may be either free or combined), the latter, on the assumption that, according to the dissociation theory, even the purest water must contain free hydrogen ions in a minute though definite amount, about one gramme in $(10)^7$ litres (Cushman and Gardner, *The Corrosion and Preservation of Iron and Steel*), maintains that this small concentration is capable of commencing the process of corrosion, and that in consequence the presence of an acid is unnecessary, the water itself being to some extent acid in character. This illustrates more clearly the essential unity of the two theories. Whichever be accepted, the general interpretation of the phenomena of corrosion will remain unaltered. Carried beyond the point of actual initiation, both theories proclaim the process to proceed electrochemically, and this term has received increasing favour as the one which best expresses the modern agreement of opinion on the mechanism of corrosion. The Electro-chemical theory, or, as it has been called, the Ionic theory, embraces both the Acid and the Electrolytic theories and is applicable to all forms of corrosion of all metals and alloys in every kind of electrolyte, whether fresh water or salt, industrial liquors or effluents. Very few are the phenomena connected with corrosion which cannot be explained by it. Methods of protection and prevention suggested by its consideration are sound in conception and are, on the whole, successful. Where they fail, the reason can be found also by an intelligent interpretation of the theory. As a practical working hypothesis there appears to be little doubt that it is the soundest and most rational theory we have, and that it is the one most likely to retain its prominence and to direct attention towards its further development and amplification.

Of the various processes by which metals deteriorate, corrosion is the most pernicious and the one which is the most difficult to prevent or alleviate. In the majority of cases also, it is the one which leads to the most rapid destruction of metals, particularly of iron and steel. It is an inherent tendency of iron to rust, and it seems doubtful if this will ever be entirely overcome. No one will dispute the importance which attaches, therefore, to a complete understanding of the process, to the production of non-corrodible, or at any rate of more resistant metals, and to the evolution and perfecting of protective measures.

It has often been remarked that the modern irons and steels and metals generally are less resistant to the attack by natural forces than were those produced by the ancients or even those of a decade ago. To some extent this is no doubt true, one reason being that modern methods of production and of working the material are more likely to enhance a condition of internal strain in the metal, and this is known to increase its susceptibility to corrosion. Also, manufacture on an ever-increasing scale multiplies the difficulties of ensuring efficient process control, and there frequently results a heterogeneous and segregated structure which likewise lowers the resistivity of the product. It must be admitted that many excellently preserved iron articles exist in such countries as Egypt and India, etc., and that they have withstood marvellously well the action of the atmosphere there for many hundreds and even thousands of years. It has nevertheless been recorded (Rosenhain, *Trans. Faraday Soc.*, Vol. XI., 1915) that samples of such material, when brought to this country and submitted to the action of our atmosphere, corrode equally as rapidly as many of our modern products. Local conditions play an important part in the corrosion of iron, etc., chief amongst these, and one characteristic of this country, is the excessive humidity of the atmosphere and the attendant other physical conditions whereby this moisture may condense in liquid form upon metals. Only

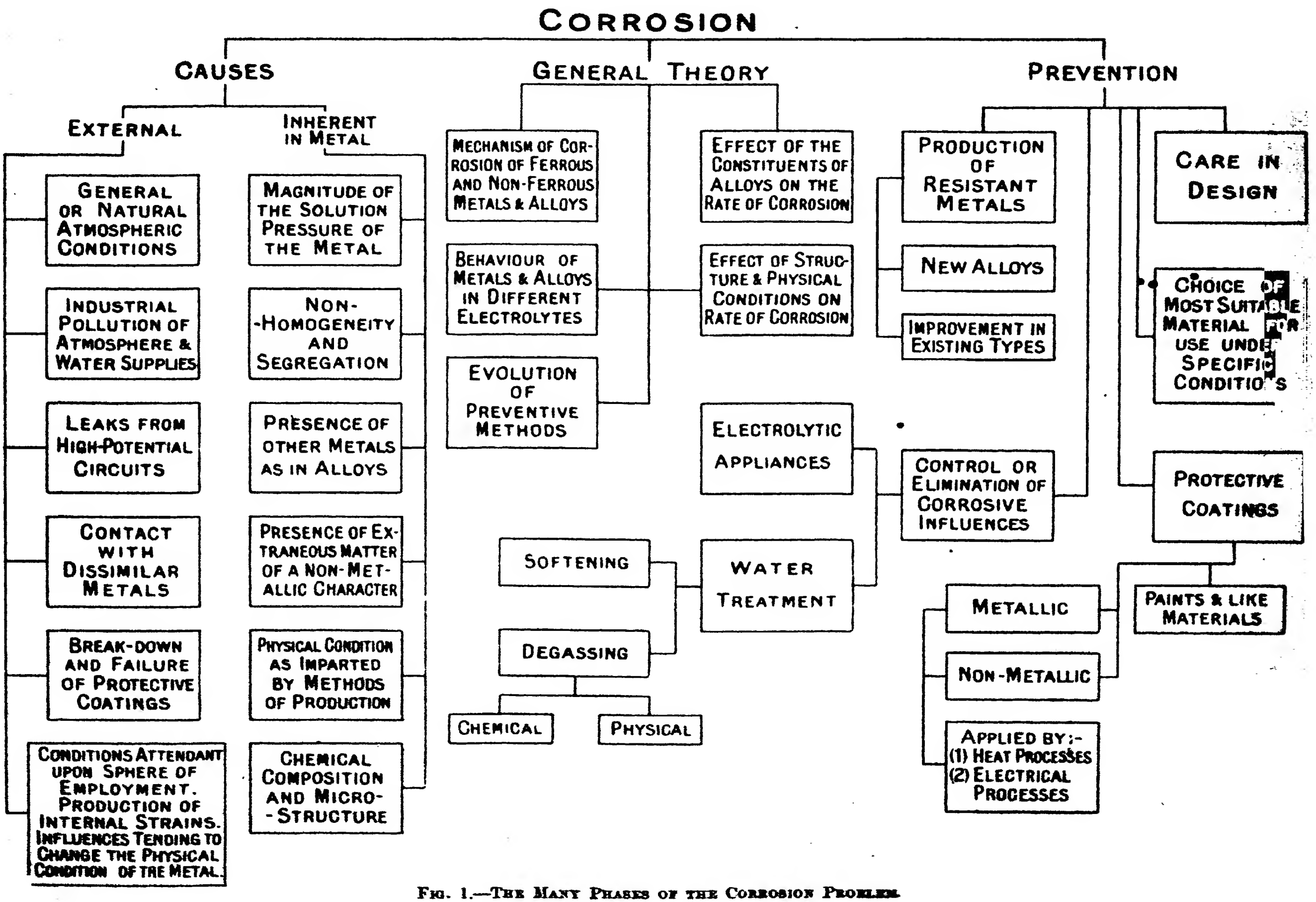
CORROSION
CAUSES
EXTERNAL
GENERAL OR NATURAL ATMOSPHERIC CONDITIONS
INDUSTRIAL POLLUTION OF ATMOSPHERE & WATER SUPPLIES
LEAKS FROM HIGH-POTENTIAL CIRCUITS
CONTACT WITH DISSIMILAR METALS
BREAK-DOWN AND FAILURE OF PROTECTIVE COATINGS
CONDITIONS ATTENDANT UPON SPHERE OF EMPLOYMENT. PRODUCTION OF INTERNAL STRAINS. INFLUENCES TENDING TO CHANGE THE PHYSICAL CONDITION OF THE METAL.
INHERENT IN METAL
MAGNITUDE OF THE SOLUTION PRESSURE OF THE METAL
NON-HOMOGENEITY AND SEGREGATION
PRESENCE OF OTHER METALS AS IN ALLOYS
PRESENCE OF EXTRANEOUS MATTER OF A NON-METALLIC CHARACTER
PHYSICAL CONDITION AS IMPARTED BY METHODS OF PRODUCTION
CHEMICAL COMPOSITION AND MICRO-STRUCTURE
GENERAL THEORY
MECHANISM OF CORROSION OF FERROUS AND NON-FERROUS METALS & ALLOYS
BEHAVIOUR OF METALS & ALLOYS IN DIFFERENT ELECTROLYTES
EVOLUTION OF PREVENTIVE METHODS
EFFECT OF THE CONSTITUENTS OF ALLOYS ON THE RATE OF CORROSION
EFFECT OF STRUCTURE & PHYSICAL CONDITIONS ON RATE OF CORROSION
PREVENTION
PRODUCTION OF RESISTANT METALS
NEW ALLOYS
IMPROVEMENT IN EXISTING TYPES
CARE IN DESIGN
CHOICE OF MOST SUITABLE MATERIAL FOR USE UNDER SPECIFIC CONDITIONS
CONTROL OR ELIMINATION OF CORROSIVE INFLUENCES
ELECTROLYTIC APPLIANCES
WATER TREATMENT
SOFTENING
DEGASSING
CHEMICAL
PHYSICAL
PROTECTIVE COATINGS
PAINTS & LIKE MATERIALS
METALLIC
NON-METALLIC
APPLIED BY:-
(1) HEAT PROCESSES
(2) ELECTRICAL PROCESSES

Fig. 1.—The Many Phases of the Corrosion Problem.

in liquid form does moisture cause corrosion. Other local corrosive influences owe their origin to the steady increase in industrial establishments whereby the atmosphere and water supplies are polluted with waste gases and effluents. In addition, cases of rapid corrosion may often be traced to the effect of stray currents from high potential circuits.

The study of corrosion is one of many phases, as may be seen from fig. 1, which represents diagrammatically the more essential features of the three chief aspects of the problem, namely, the general theory, the practical causes and influences by which corrosion is initiated and accelerated, and the methods by which it is attempted to arrest or reduce its violence. Each single item enumerated might form the subject of years of research, and it is only by a well-organised campaign of investigation into these numerous branches that a complete or satisfactory control of the phenomena will be possible, and until we attain this the economy of our metals and the conservation of our natural resources will remain an imperfectly solved problem.

CHAPTER II

THE THEORY OF CORROSION

ANY acceptable theory of corrosion must be capable of explaining three fundamental facts namely:—

1. That iron will not corrode or rust in dry air, that is, in the absence of moisture.

2. That iron will not rust in moist air provided the conditions of temperature are such that no liquid water can condense on its surface.

3. That iron will not rust in pure liquid water if air is completely excluded.

Several theories have been advanced from time to time in attempts to explain the initiation and process of corrosion; but, as knowledge of the subject has expanded, two only of them have survived the severe criticisms to which they have been subjected. These are, as already indicated, the Acid Theory and the Electrolytic Theory. Since they each have a common basis of interpretation, it may be desirable before proceeding to their further discussion, to include a brief review of several phenomena, upon the knowledge of which depends a clear understanding of most of the problems presented by the study of corrosion.

Solution and Osmotic Pressures. When a soluble material dissolves in water its molecules distribute themselves equally throughout the mass of the liquid, and the force by which this is accomplished is known as the "solution pressure." The reaction to this force, and which tends to prevent the solution or equi-spatial distribution of the molecules of the dissolving body, is called the "osmotic pressure." It may readily be conceived that, at the instant before solution commences, the solution pressure of the substance is at a maximum and the osmotic, or opposing pressure, at a minimum, and that as solution proceeds the magnitudes of these two forces gradually approach a common value. When this point of equilibrium is reached, further solution of the substance will cease. In other words, when the solution and osmotic pressures balance, the substance exhibits its maximum solubility and the water will be saturated with respect to that particular substance and to the physical conditions of temperature and pressure prevalent at the time. Any external factor which, acting on the system, tends to lower the osmotic pressure will increase the extent of the solubility of the substance, and if the supply of the latter and of the water be maintained, the permanent presence of an osmotic pressure-reducing influence will result in a continued solution of the substance. The importance and direct bearing of this on corrosion will become apparent later.

As usually understood, the term solubility would make a sharp distinction between such materials as, for instance, soda and iron or stone; actually the terms solubility and insolubility are relative only, since it is doubtful whether any substance exists upon which water has not some solvent action. The magnitudes of the solution and osmotic pressures in the case of bodies usually classed as soluble may be very considerable. Pfeffer has shown that in the case of a 6 per cent. solution of sugar the osmotic pressure at 14° C. is equivalent to 60 pounds per square inch. The solution pressure will have a correspondingly high value, and although sugar is relatively very soluble, yet it is indisputable that the so-called insoluble bodies, like iron, etc., must have solution pressures of small though definite magnitude.

Electrolytic Dissociation.—One of two things may occur when a substance dissolves in water, either the solution becomes a conductor of electricity or it retains its original non-conductive character. A solution of sugar in water is illustrative of the latter. Acids, bases, and salts confer the former property on their solutions, and they effect this by splitting up or dissociating into atoms or groups of atoms which carry charges of static electricity. Such electrically charged atoms, etc., are known as "ions," and the dissociation whereby they are produced may be simply expressed in the following manner:—

$$(1)\quad \begin{array}{ccccc} \text{Hydrochloric acid} & = & \text{Hydrogen ions} & + & \text{Chlorine ions} \\ HCl & & H^{\cdot} & & Cl' \end{array}$$

$$(2)\quad \begin{array}{ccccc} \text{Calcium hydrate} & = & \text{Calcium ions} & + & \text{Hydrate ions} \\ Ca(OH)_2 & & Ca^{\cdot\cdot} & & OH' \quad OH' \end{array}$$

$$(3)\quad \begin{array}{ccccc} \text{Sodium sulphate} & = & \text{Sodium ions} & + & \text{Sulphate ions} \\ Na_2SO_4 & & Na^{\cdot} \quad Na^{\cdot} & & SO_4'' \end{array}$$

The nature of the charge carried by an ion is indicated by the small $^{\cdot}$ or $'$ sign placed above the symbol and the relative magnitudes of the charges by the number of $^{\cdot}$ or $'$ signs. Thus, the negative charge carried by a sulphate ion, SO_4'', is just double that carried by the negatively charged chlorine ion, Cl'. The ions resulting from the solution of a compound are always of two kinds, "cations," carrying positive charges, and "anions" carrying negative charges, and in solution the sum of the positive charges is always numerically equal to that of the negative charges. That is to say, the charges of opposite sign balance or neutralise each other so that a dissolved substance does not confer a definite potential on its solution. All acids in solution are characterised by the hydrogen cation and all bases by the hydrate or hydroxyl anion. It must be remembered that the properties of an ion do not correspond with those of the uncharged atom; metallic or atomic sodium, for example, cannot exist as such in the presence of water, but the charged atom or ion can and does.

There are other ways in which ions may be produced, one of which is by the transference or exchange of the charge from an already existing ion to an atom. Perhaps the simplest example of this is the solution of zinc in an acid which proceeds in the following manner:—

$$(4)\quad \begin{array}{ccccccccc} \text{Zinc} & + & \text{Hydrochloric acid} & = & \text{Zinc ions} & + & \text{Chlorine ions} & + & \text{Hydrogen} \\ Zn & + & \begin{array}{c} H^{\cdot}\,Cl' \\ H^{\cdot}\,Cl' \end{array} & = & Zn^{\cdot\cdot} & + & \begin{array}{c} Cl' \\ Cl' \end{array} & + & H_2(\text{gas}) \end{array}$$

The hydrogen ions, resulting from the ionic dissociation of the hydrochloric acid, have transferred their charges to the metallic zinc, thereby becoming atomic, and as such insoluble. They escape as gas bubbles from the surface of the zinc, the atoms of which, by acquiring charges, have entered solution as zinc cations. It is thus easy to visualise the solution of a relatively insoluble material, such as a metal, which may dissolve directly from the metallic condition, and this type of action, which will subsequently be referred to again in more detail, should be borne in mind when considering the Acid and Electrolytic theories of corrosion. A further instance of the solution of a metal by the transference of charges from ions to atoms is the well-known precipitation of copper from solution by metallic iron :—

$$(5)\quad \begin{array}{ccccccc} \text{Copper sulphate} & + & \text{Iron} & = & \text{Iron sulphate} & + & \text{Copper} \\ Cu^{\cdot\cdot}\,SO_4'' & & Fe & & Fe^{\cdot\cdot}\,SO_4'' & & Cu \\ & & \text{(atomic)} & & & & \text{(atomic)} \end{array}$$

This act of interchange or exchange of charge, as shown above, is, of course, primarily electrical, but since the result is manifested by a chemical change, a process of this or an analogous type justifies its consideration as an electro-chemical one, and since the corrosion of metals proceeds by such processes, the electro-chemical conception of corrosion would appear to be rational.

A third method of ion formation is that in which two atoms of dissimilar elements change into ions by mutual contact. A solution of chlorine in water contains this element in the atomic form ; if a strip of gold-leaf is placed in this solution it dissolves and produces positively charged ions, and at the same time the chlorine becomes ionic so that a balance between the charges on the gold cations and those on the chlorine anions is effected :—

$$(6)\quad \begin{array}{ccccccc} \text{Gold(atomic)} & + & \text{Chlorine(atomic)} & = & \text{Gold(ionic)} & + & \text{Chlorine(ionic)} \\ Au & & 3Cl & & Au^{\cdot\cdot\cdot} & & Cl' + Cl' + Cl' \end{array}$$

Lastly, there is the production of ions by the conversion of an atom to an ion accompanied by the increasing of the charge carried by an already existing ion. If chlorine gas is bubbled through a solution of ferrous chloride, a reaction occurs in which the ferrous cation, carrying two positive charges, is converted into a ferric cation carrying three positive charges, whilst the chlorine simultaneously changes from the atomic to the ionic condition :—

$$(7)\quad \begin{array}{ccccc} \text{Ferrous chloride} & + & \text{Chlorine} & = & \text{Ferric chloride} \\ Fe^{\cdot\cdot}\,Cl'\,Cl' & & Cl & & Fe^{\cdot\cdot\cdot}\,Cl'\,Cl'\,Cl' \\ & & \text{(atomic)} & & \end{array}$$

These four methods of ion formation may each represent some process intimately connected with the practical phenomena of corrosion.

Electrolysis and Polarisation.—It was stated that when the solution of a substance in water resulted in its dissociation into ions, the system became a conductor. If a current is passed through such a solution by means of suitable electrodes a phenomenon known as electrolysis occurs, and it consists primarily of a mechanical movement or migration of the ions. The cations migrate to the negative electrode, or cathode, and the anions to the positive electrode, or anode. They surrender their respective charges to the electrodes and become atomic; and they may then leave the system by escaping as bubbles of gas, as in the case of the electrolysis of hydrochloric acid, or by plating out on the electrodes in the metallic form, as, for instance, when a solution of copper sulphate is electrolysed. In other cases, the mechanism is more complex. Considering the case of a solution of sodium sulphate, there first occurs the migration of the sulphate and sodium ions to their respective electrodes and their subsequent discharge. Metallic sodium, however, cannot exist as such in the presence of water, nor can the discharged sulphate ions; in each case, therefore, secondary reactions take place between the water and the discharged ions, producing respectively sodium hydrate and sulphuric acid, and liberating hydrogen and oxygen as gases which appear on the electrodes as the products of the electrolysis. Finally, a tertiary reaction between the sodium hydrate and the sulphuric acid results in the regeneration of the sodium sulphate. The above sequence of reactions is, then, as follows:

$$(8)\ \left\{\begin{array}{ll} (a) & Na_2SO_4 \xrightarrow[\text{ionised in solution}]{} Na^{\bullet} + Na^{\bullet} + SO_4'' \\ (b) & Na^{\bullet} + Na^{\bullet} + SO_4'' \xrightarrow[\text{on migration and discharge}]{} 2Na + SO_4 \\ (c) & 2Na + SO_4 \xrightarrow[\text{react with water}]{} 2NaOH + H_2SO_4 + H_2 + O \\ (d) & 2NaOH + H_2SO_4 \xrightarrow[\text{combine}]{} Na_2SO_4 + 2H_2O \end{array}\right.$$

The amount of sodium sulphate remains undiminished, though its concentration increases, of course, owing to the elimination of the elements of water, as shown in (*c*).

Electrolysis may also take place without the aid of an externally applied current. If two dissimilar metals are partially immersed in the electrolyte and electrically connected externally by a wire, a current will be generated at the expense of the more electro-positive metal, or, in other words, of the metal having the higher solution pressure. This metal expels positively charged ions from its surface into the liquid medium and becomes itself negatively charged, so that the dissolving metal appears as the negative pole of the external portion of the circuit. It is not necessary even that the two metals be externally in electrical contact; if they are placed in contact in the solution the same process will proceed, the solution in this case taking the place of the wire. Current will flow from the more electro-positive metal, through the solution, to the less electro-positive metal. Commercial metals are usually of sufficiently composite a structure, owing to the presence of impurities and segregation, etc., that adjacent areas on their surfaces have different electrolytic solution pressures or potentials and when in contact with an electrolyte the metal behaves as if it were a mosaic of dissimilar metals; currents are established between adjacent areas of the surface, those having the higher potential dissolving preferentially to those of lower potential. That form of corrosion usually known as "pitting" is often readily explained from such considerations as the above.

When a metal dissolves in an acid medium the conversion of the metal to the ionic condition will occur by the exchange of charges between the hydrogen ions and the metal, as shown in equation (4), whilst in a neutral medium the metallic ions derive their charges from the electrode or bulk of the metal which becomes negatively charged. In an almost neutral medium a combination of these two results takes place and the evolution of gas is too slow to be visible. Such a condition leads to polarisation, and by an almost neutral medium is inferred a solution in which the concentration of hydrogen ions is relatively low. Polarisation is essentially the plating of the dissolving metal with a film of charged ions. If we consider the academic case of a strip of pure iron in pure water, which latter we will assume to be dissociated to a small degree into hydrogen and hydroxyl ions, then the following sequence, analogous to the above, occurs: By reason of its solution pressure the iron shoots off from its surface a number of positively charged ferrous ions into the water, thus disturbing the electrical balance between the already present hydrogen and hydroxyl ions. As a result, the positive ion whose element has the lower solution pressure, or which is the less electro-positive, is displaced, and in this case the hydrogen ions surrender their charges to the iron strip and adhere to it in the form of a gaseous film, thereby restoring the balance between ionic charges. A galvanic current will thus flow from the iron strip via the ferrous ions in solution and back again via the hydrogen ions to the undissolved metal. The gaseous film of hydrogen deposited on the latter is, however, a very poor conductor and offers a high resistance to this current, so that before long the circuit is effectively broken. Further solution of the iron is thus prevented by the polarising effect of this gaseous film, and will not recommence until the latter is removed, that is, until some depolarising agent is brought into play.

Before leaving the consideration of these phenomena there are two others which merit some attention, since they are very intimately associated with many of the problems presented by the corrosion and preservation of metals. These are "Oxidation" in solution and the reverse process of "Reduction," and "Hydrolysis."

Oxidation.—Referring to equation (7), we have the instance of the conversion of ferrous chloride into ferric chloride, a compound whose molecule on dissociation yields a ferric cation carrying three positive charges as compared with the two positive charges carried by the original ferrous ion. The total amount of iron has not been increased, that of the chlorine or negative radicle of the compound has. This type of process is termed "Oxidation," and it involves (*a*) the increasing of the proportion of the electro-negative radicle of a compound, and (*b*) the increasing of the magnitude of the charge carried by the electro-positive radicle or ion. For most practical purposes the charges carried by an ion may be regarded as synonymous with valency; hence a ferrous ion, $Fe^{\cdot\cdot}$, carrying two charges is divalent and a ferric ion, $Fe^{\cdot\cdot\cdot}$, carrying three charges is trivalent. The second change involved by oxidation may therefore be alternatively regarded as increasing the valency of the electro-positive radicle. Processes which result in a decrease in this valency are those of "Reduction."

Hydrolysis.—It is generally known that salts produced by the combination of a strong base with a weak acid impart basic reactions to their solutions, whilst the solutions of salts resulting from the combination of a strong acid with a weak base are acidic in character. The phenomenon whereby the characteristics of the stronger radicle are developed is that of "Hydrolysis," and the following example may serve to illustrate the process :—

$$\text{(9)}\quad \begin{array}{llll} \text{Sodium carbonate} + \text{Water} & = \text{Sodium hydrate} & + \text{Carbonic acid} \\ Na_2CO_3 + H_2O & = 2NaOH & + H_2CO_3 \end{array}$$

The sodium hydrate produced has a very high solution pressure and is therefore very strongly ionised (or completely dissociated into sodium and hydrate ions). The hydrate ions confer a basic reaction to the solution, which the carbonic acid, because of its very low degree of dissociation failing to produce a sufficiency of hydrogen ions, cannot neutralise. In this way the salt, sodium carbonate, instead of yielding a neutral solution, as the name "salt" would imply, gives an alkaline solution. The hydrolysis of aluminium sulphate, on the other hand, yields an acid solution :—

$$\text{(10)}\quad \begin{array}{llll} \text{Aluminium sulphate} + \text{Water} & = \text{Aluminium hydroxide} & + \text{Sulphuric acid} \\ Al_2(SO_4)_3 + 6H_2O & = 2Al(OH)_3 & + 3H_2SO_4 \end{array}$$

In this case the acid product of hydrolysis is strongly ionised and the aluminium hydroxide, being insoluble, is not ionised at all.

THE THEORY OF CORROSION

No useful purpose would be served by entering into a detailed discussion of the relative probabilities of the two principal theories of corrosion. It has already been pointed out that the final acceptance or rejection of either will not alter the interpretation of corrosion as it occurs in practice. Whilst the author inclines to the belief that the Acid theory should receive preference academically, he is content to leave the final verdict to the reader, who may follow the respective claims of these two theories by referring to the works of Friend (*The Corrosion of Iron and Steel*), and of Cushman and Gardner (*The Corrosion and Preservation of Iron and Steel*), who discuss and criticise them in considerable detail, and who, although they reach conclusions which are academically opposed, yet agree that, from a practical point of view, the phenomena of corrosion are explained most satisfactorily on an electro-chemical basis. It is proposed, therefore, to consider these theories conjointly with reference to this basis.

The Acid and Electrolytic Theories.—The formulation of the Acid theory is generally attributed to Crace Calvert, and it presumes that pure liquid water and pure oxygen are not alone sufficient to initiate the corrosion of pure iron, but that a third factor is necessary. Calvert has been vigorously supported by Crum Brown,

Moody, and Friend, and as vigorously attacked by Dunstan, Whitney, Tilden, Cushman, and others. This third factor, necessary to the initiation of the corrosion of iron, is the presence of an acid. It may be a feebly ionised acid like carbonic acid, or it may be in the combined form, whence, by hydrolysis, the characteristic hydrogen ion may be produced.

The quantity of acid necessary is infinitesimal, since, according to the Acid theory, one molecule of acid will suffice to corrode an unlimited amount of metal. The acid usually taken to illustrate this theory is carbonic acid, because of its universal presence in all atmospheres and waters. In short, then, the third factor implies the presence of hydrogen ions. The Electrolytic theory states that an acid as such is not essential in any form, either free or combined, but that the solution pressure of pure iron in pure water results in the formation of ferrous ions and in the consequent discharge of an equivalent number of hydrogen ions which are assumed to exist even in the purest water. Although hydrogen is a gas, yet it is electrically in the same category as the metals, being electro-positive, and, as shown in equation (4), an exchange of charge can take place between its ions and the atoms of the more electro-positive iron. Each theory, therefore, explains the primary or initial attack upon the iron as the result of attack by hydrogen ions, and they differ merely in the fact that they presume the presence of these ions to originate from different sources.

Proceeding beyond the point of initiation, the compatibility of these two theories is further demonstrated in that they both regard the presence of oxygen as essential to the continuation of the process. The Acid theory, viewing corrosion as a cyclic process, in which a minute amount of acid may corrode an infinite quantity of metal (in a manner which may be looked upon as catalytic), explains the process by the following sequence: Firstly, the attack by the acid, for example carbonic acid, on the iron results in the production of a ferrous salt, in this case ferrous carbonate:—

$$(11)\quad 2Fe + 2H_2CO_3 = 2FeCO_3 + 2H_2$$

Secondly, the ferrous carbonate is acted upon by oxygen in the presence of water and is converted into the insoluble ferric hydroxide which is precipitated from the system. This is accompanied by the simultaneous regeneration of the original quantity of carbonic acid:—

$$(12)\quad 4FeCO_3 + O_2 + 10H_2O = 4Fe(OH)_3 + 4H_2CO_3$$

and the oxidation of the hydrogen produced in equation (11) to water. The cycle is thus completed and corrosion will continue so long as the supply of oxygen required in equation (12) is maintained. It will be noted that in equation (11) gaseous hydrogen is set free, and this may be regarded as analogous to the liberation of hydrogen by the discharge of hydrogen ions in the explanation offered by the Electrolytic theory, which is equally as simple and straightforward as the one just illustrated. The first stage in the mechanism of the corrosion of pure iron by pure water and pure oxygen only is the transfer of charges from hydrogen ions to the metal. The latter *thereby enters solution and continues to do so until the polarisation, due to the film of gaseous hydrogen deposited on the metal surface, is sufficient to arrest the process. This stage may be represented by :—*

$$(13)\ Fe + \frac{H^{\cdot}OH'}{H^{\cdot}OH'} = Fe^{\cdot\cdot}\frac{OH'}{OH'} + H_2\,(gaseous)$$

The liquid medium at this point is virtually a solution of ferrous hydroxide, $Fe(OH)_2$, ionised, of course, and the second stage consists in the oxidation and precipitation of this as ferric hydroxide or rust :—

$$(14)\ 4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3$$

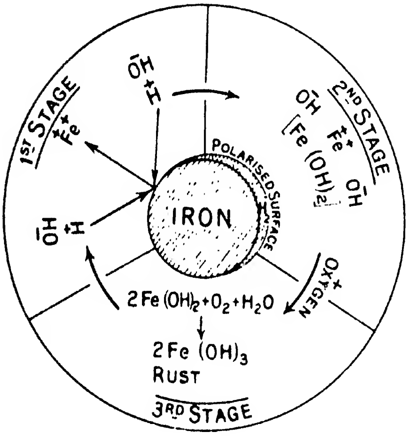
1ST STAGE
$\overset{+}{Fe}$
$\overset{-}{OH}$
$\overset{+}{H}$
$\overset{-}{OH}$ $\overset{+}{H}$
IRON
POLARISED SURFACE
H
2ND STAGE
$\overset{-}{OH}$
$\overset{+}{Fe}$
$\overset{-}{OH}$
$[Fe(OH)_2]$
OXYGEN
$2Fe(OH)_2+O_2+H_2O$
$2Fe(OH)_3$
RUST
3RD STAGE

FIG. 2.—GRAPHIC REPRESENTATION OF THE ELECTROLYTIC THEORY OF CORROSION.

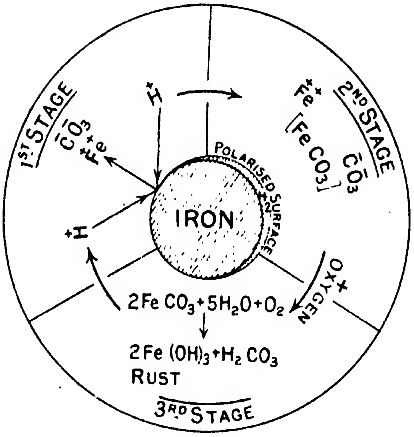
1ST STAGE
$\overset{-}{CO_3}$
$\overset{+}{Fe}$
$\overset{+}{H}$
$\overset{+}{H}$
IRON
POLARISED SURFACE
H_2
2ND STAGE
$\overset{+}{Fe}$
$[Fe\,CO_3]$
$\overset{-}{CO_3}$
OXYGEN
$2Fe\,CO_3+5H_2O+O_2$
$2Fe(OH)_3+H_2CO_3$
RUST
3RD STAGE

FIG. 3.—GRAPHIC REPRESENTATION OF THE ACID THEORY OF CORROSION.

This precipitation of ferric hydroxide disturbs the equilibrium of the system, and, in conjunction with the second effect of the oxygen, which, by combining with and removing the polarising film of hydrogen, depolarises the metal surface, results in the continued solution or corrosion of the metal. The entire process may be visualised by referring to fig. 2, in which it is presented schematically. In the first stage we have the metal shooting off ions into the water and the development of the polarising film of hydrogen gas. This continues until stopped by the polarisation, and we have the condition represented by stage two, in which the liquid is virtually a solution of ferrous hydroxide. In the third stage occurs the oxidation of the ferrous ions and their precipitation as rust, and also the depolarisation of the metal surface. This brings us back again to the beginning of the cycle. Fig. 3 shows the sequence, depicted in a similar manner, as explained by the Acid theory, and its comparison with fig. 2 will further indicate the futility of continuing from a practical point of view, the controversy between the two theories. It can have no apparent useful conclusion, nor is it likely to help in the solution of problems involved in the practical preservation of our metals.

A conclusion, which may be regarded as an amplification of the Acid theory, has been reached by Paul (*Boiler Chemistry and Feed-water Supplies*), who, as a result of his investigations, states that in the presence of an excess of carbonic acid, free or atmospheric oxygen is not essential to corrosion. He explains the process under these conditions as follows:

(15) $4Fe + 4H_2CO_3 = 4FeCO_3 + 4H_2$

(16) $4FeCO_3 + 10H_2O = 4Fe(OH)_3 + 2H_2CO_3 + 2H.COOH$ (formic acid)

(17) $Fe + 2H.COOH = Fe(CHO_2)_2 + H_2$

(18) $2Fe(CHO_2)_2 + 2H_2 + 3H_2O = 2Fe(OH)_3 + 3H.CHO + H.COOH$

The first reaction is straightforward and results simply in the production of ferrous carbonate and gaseous hydrogen. In the second stage, equation (16), the ferrous carbonate is decomposed by water into ferric hydroxide, and this is accompanied by the regeneration of one half of the original quantity of carbonic acid and the production of formic acid. The regenerated carbonic acid attacks more metal, and the formic acid is responsible for the production of ferrous formate as shown in equation (17). Finally, the ferrous formate is acted upon by the gaseous hydrogen evolved in equations (15) and (17), yielding ferric hydroxide and some formaldehyde and regenerating formic acid, equation (18). It will be noted that during this sequence the carbonic acid is continually being halved in quantity and the formic acid, first produced in equation (16), is reduced to 25 per cent. of its original concentration. For corrosion to proceed in this way, *i.e.*, in the absence of atmospheric oxygen, the supply of carbonic acid must therefore be maintained, and its action is not to be compared with the catalytic-like action of a trace of carbonic acid as explained by the Acid theory proper.

Paul's suggestion, as applicable to special conditions, has much to substantiate it; the reduction, in aqueous solution, of carbonic acid to formaldehyde has been effected by Fenton (*Trans. Chem. Soc.*, 1907, **91**, 687), and the reduction is accelerated by the presence of ferric hydroxide. Also there would appear to be little doubt that when an excess of carbonic acid acts on iron, organic compounds are produced which may be regarded as reduction or degradation products of carbonic acid. It seems possible also that the formation of these compounds may be accompanied by an evolution of oxygen, and should this be so, the equations 15-18 might be modified to approach more closely to the Acid theory, in that the oxidation of the ferrous compounds to ferric hydroxide could be considered as effected directly by this oxygen. More evidence is necessary, however, before such an explanation as the above can be extended to cases of general atmospheric corrosion.

The Colloid Theory of Corrosion.—Although the electro-chemical conception of corrosion is applicable to the interpretation of practically all phenomena connected with the various processes by which corrosion may occur or by which it may be accelerated or retarded, yet there are some few instances in which it fails satisfactorily and completely to explain the facts observed. A consideration of these cases, supported by much experimental evidence, has led Friend (*Trans. Chem. Soc.*, 1921, **119**, 932, and *The Corrosion of Iron*, Carnegie Scholarship Memoirs, Vol. XI., 1922) to suggest a new theory, which not only explains these cases fully, but which may also be extended to the processes of corrosion generally, and offers in many *instances an alternative explanation of the phenomena involved. This theory does not repudiate the fundamental principles of the electro-chemical mechanism of corrosion, but, by the application of a new hypothesis to certain stages of the* process of the corrosion of iron, permits a more comprehensive explanation.

It will be convenient to discuss at this point some of the properties of colloids which have an important bearing on Friend's theory.

The study of colloids dates back to 1851, when Graham (*Phil. Trans.*, 1861, **151**, 183, and *Annalen*, 1851, 77, 56) drew attention to the difference between the diffusive properties of those substances which can be readily crystallised from water, such as inorganic salts generally, and those which cannot be obtained in a crystalline form, or only with great difficulty. Of the latter class, gums and gelatine are typical examples, and the designation "colloid" was originally suggested by the Greek word meaning glue. This class is characterised by the inability of the substances included in it to pass, or diffuse, through animal and vegetable membranes. This negative property is made use of in the separation of colloids from substances in the first class, or crystalloids. The former are retained by the membrane whilst the crystalloids diffuse through it. The process is known as "dialysis."

The modern application of the word "colloid" infers a particular physical condition, in which form it is now possible to obtain many substances, and not, as originally, to a definite class of materials. Thus a colloidal solution is now understood to indicate, not necessarily a solution of gelatine or glue, but any solution which possesses specific properties comparable with those of a gelatine solution. Colloidal solutions of hydroxides of iron, of sulphur, arsenious sulphide, metals and metallic salts, etc., are more or less readily prepared.

A solution of a colloid differs in many respects from that of a crystalloid or true solution; the osmotic pressure of the system is extremely small in comparison with the quantity of substance which may be present, and the colloid has little, if any, influence as regards depressing the freezing point or elevating the boiling point of the liquid medium. There exists very strong evidence that colloidal solutions, particularly those in which we are interested in this connection, are really suspensions in the liquid of extremely minute solid particles, which are retained in suspension by the tenacity of the medium. The size of the particles we may here regard as intermediate between those in a mechanical suspension and those in a true or crystalloidal solution, which latter are, of course, of molecular dimensions. The fluid in which the colloid is suspended is known as the "dispersion" medium, and the colloid as the "dispersoid." One essential difference between a true solution and a colloidal solution is that the latter is a two-phase system and the former a single-phase system.

The two properties of colloids which have the most significance in regard to Friend's theory are their behaviour in an electrical field and their coagulation or precipitation from solution, or rather from suspension, by certain agents.

If a current is passed through a colloidal solution by means of two electrodes, a migration of the dispersoid occurs which may be looked upon as analogous to that of the ions in a true solution. *In this case, however, the mechanical movement is in one direction only, either to the cathode or to the anode, depending on the nature* of the colloid. There is good reason to justify the assumption that the particles of a substance, when in colloidal solution, carry electrical charges, those colloids which migrate to the anode bearing negative charges and those which migrate to the cathode carrying positive charges. Ferric hydroxide is one of the latter and is therefore considered to be an electro-positive colloid.

Colloids may be precipitated from their solutions by the addition of compounds which undergo ionic dissociation in the dispersion medium, *i.e.*, acids and salts, etc., and from their behaviour in the presence of such compounds it is possible to divide them into two groups:

> (1) "Suspension" colloids. These give non-viscous solutions and are precipitated by small quantities of electrolytes. They can be restored to a colloidal condition only by indirect or roundabout means, and are, in consequence, also referred to as "irreversible" colloids.
>
> (2) "Emulsoid" colloids. These give viscous solutions and are not so readily precipitated by electrolytes. They may be brought into colloidal solution again by simple contact with water, and are therefore called "reversible" colloids.

The first class is the one with which we are chiefly concerned. The precipitation is effected by very small quantities of electrolytes and seems to occur by a neutralisation of the charges carried by the colloidal particles by those ions of the dissociated electrolyte having the opposite sign. Thus an electro-positive colloid will be precipitated by the electro-negative ion of a salt in solution, that is, by the acid radicle. On the other hand, an electro-negative colloid will be precipitated by an electro-positive ion or basic radicle. Further evidence in this direction is to be found in the fact that colloids whose charges are presumably of opposite sign precipitate each other.

Small though the concentration of electrolyte necessary to precipitate a colloid may be, yet it has a minimum value, below which precipitation is not effected. This minimum value has been found to be of the same order for all electrolytes in which the precipitating radicles have the same valency. Thus the minimum concentrations of monovalent acid radicles required to precipitate an electro-positive colloid will be identical irrespective of whether the radicle is a chloride, nitrate, or bromide. Further, the higher the valency of the precipitating ion the lower its minimum concentration. The requisite quantity of a divalent ion is therefore less than that of a monovalent ion, but greater than that of a trivalent ion.

This very brief outline of some colloidal properties will suffice as a preface to the following description of Friend's theory.

Friend's Colloid theory appears to have resulted chiefly from an examination of two apparent anomalies. When iron corrodes in moving water the rate of corrosion is influenced in an unexpected manner by the rate of flow of the water over the metal surface. As the rate of flow is increased the corrosion is at first rapidly accelerated until it reaches a maximum. After this, however, further increase in the velocity of the water is accompanied by a decrease in the rate of corrosion until the latter appears to be entirely arrested, and the only destructive influence to which the iron seems to be exposed is the mechanical erosion by the rapidly moving water. The results of Friend's experiments are reproduced graphically in fig. 4. Corrosion is seen to reach a minimum at a water velocity of about two miles per hour, after which corrosion, as indicated by observations based on losses in weight, slowly increases. Since, however, visible evidence of corrosion is lacking at these velocities, in that no rust appears, this increase may be looked upon as the effect of mechanical erosion.

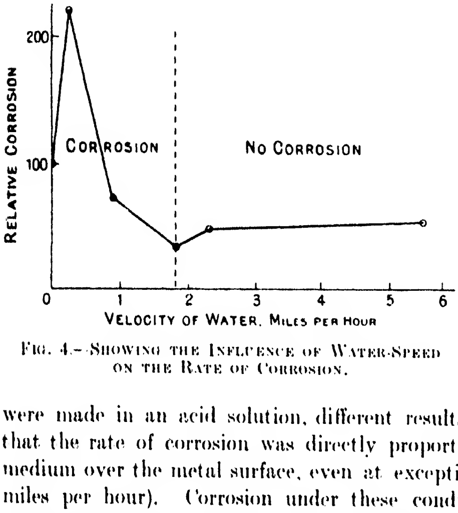

FIG. 4.—SHOWING THE INFLUENCE OF WATER-SPEED ON THE RATE OF CORROSION.

When similar observations were made in an acid solution, different results were obtained, and it was found that the rate of corrosion was directly proportional to the velocity of the acid medium over the metal surface, even at exceptionally high velocities (over thirty miles per hour). Corrosion under these conditions is therefore accelerated by increasing the velocity of the medium and not, as in the case of water, reduced. Also it was found that at a given velocity the rate of corrosion was almost constant, no matter what the concentration of the acid might be.

These apparently contradictory observations are difficult, if not impossible, to explain by the theory of corrosion as hitherto described. Friend, however, has very recently offered the following suggestions :-

(1) In contact with water and air the iron is primarily oxidised to ferrous hydroxide which is produced in the colloidal or "sol" condition.

(2) This colloidal ferrous hydroxide is then oxidised by the presence of excess of air to ferric hydroxide, which also is produced in the colloidal form.

(3) The colloidal ferric hydrate then acts as a catalyst and accelerates

the oxidation of more iron by itself undergoing reduction to the colloidal ferrous hydrate or hydroxide, but is immediately re-oxidised as in (2).

(4) The product of corrosion, or rust, appears as the ferric hydroxide sol flocculates or precipitates out of solution.

Corrosion in water would proceed by this theory in two ways, one being a simple process of solution and the other a catalytic process, the catalyst being a product of the corrosion of the iron. In water or neutral media, the catalytic process will predominate and the rate of the formation of the catalyst colloid will largely determine the rate of corrosion. In an acid medium the process of simple solution will obviously predominate.

The explanation of the different behaviours of iron in neutral and acid media is now clear. Rapid motion of a neutral medium will remove the catalysing colloid from the iron surface as rapidly as it is formed, and consequently the corrosion is retarded. Rapid movement of an acid medium will, on the other hand, accelerate the rate of solution by increasing the number of hydrogen ions which are brought into contact with the iron in a given unit of time.

This theory has much to substantiate it; any agent, whether chemical, physical, or mechanical, which will destroy or remove electro-positive colloids, such as ferric hydroxide sol, will tend to retard corrosion, whilst factors which stabilise the colloid accelerate corrosion.

The second anomaly to which Friend has applied his new theory is the influence of salt solutions of varying concentrations on corrosion. As a general rule, the presence of a dissolved salt increases the rate of corrosion, and the acceleration increases with increase in the concentration of the salt until a maximum rate is reached. Further increase in the concentration of the salt brings about a reduction in the rate of corrosion. The Colloid theory offers a very rational explanation of this, but its more detailed consideration in this connection will be reserved for a later chapter.

The Peroxide, Oxide and Biological Theories of Corrosion. The postulation of a theory usually results in a stimulation of enquiry into the particular branch of science concerned, and is therefore very often the direct cause of an expansion of knowledge on the particular subject. Even though the theory only partially explains the facts and may be soon discarded, yet the discussion which it occasions, together with the practical investigations which inevitably follow in attempts to condemn or substantiate it, bring to light new phenomena, the consideration of which results in the evolution of a new theory, sounder than its predecessor in that it offers a fuller explanation of the processes concerned. Discussion and vigorous controversy are essential to the accumulation of knowledge.

Although the following theories are no longer regarded as tenable, yet a brief representation of them should be given if only for the sake of completeness.

A certain amount of circumstantial evidence may be advanced in support of the Peroxide theory of corrosion, suggested by Dunstan, Jowett, and Goulding (*Trans. Chem. Soc.*, 1905, **87**, 1548), as the result of a long series of investigations. They concluded that water and oxygen alone were necessary for corrosion to commence and proceed, and explained the process in the following manner: An intermediate product, hydrogen peroxide, is produced during the formation of rust, and accelerates corrosion by oxidising and precipitating the ferrous hydroxide first produced, and also by itself attacking the metallic iron.

$$(19)\ 2Fe + 4H_2O = 2Fe(OH)_2 + 2H_2$$

$$(20)\ 2H_2 + 2O_2 = 2H_2O_2$$

$$(21)\ 2Fe(OH)_2 + 2H_2O_2 = 2Fe(OH)_3(\text{rust}) + H_2O_2$$

$$(22)\ Fe + H_2O_2 = Fe(OH)_2$$

$$(23)\ 2Fe(OH)_2 + H_2O_2 = 2Fe(OH)_3(\text{rust})$$

It is possible to detect traces of hydrogen peroxide when many metals corrode in water to which air has access. Dunstan and his colleagues made many experiments to obtain evidence of this kind, and although they were successful in detecting hydrogen peroxide during the corrosion of copper, mercury, lead, silver, tin, zinc, and bismuth, they failed to detect it in the case of iron. They attribute this failure to the rapidity with which the peroxide is decomposed by iron, and argue that failure to detect its presence does not necessarily preclude the possibility of its formation. There are other serious objections, however, which prevent the acceptance of this theory. In the first place, pure hydrogen peroxide in dilute solution is without action on iron, so that equation (22) cannot be accepted as truthful. Secondly, substances which will destroy hydrogen peroxide should, if the theory is correct, prevent, or at any rate retard, corrosion. Many of these substances do act in this way, but the fact that others do not is sufficient to detract from the soundness of the theory. Thirdly, it should not be assumed that the presence of a substance which destroys hydrogen peroxide will also prevent its momentary formation. If it is produced at all, then it should result in visible corrosion if the Peroxide theory is to fit the facts. Finally, it may be pointed out that the presence of hydrogen peroxide should be detectable during the corrosion of iron by the very delicate means which are at our disposal. In every case, however, negative results have been obtained.

The Oxide theory of corrosion regarded the process as one of simple oxidation, similar to that which results if iron is heated to a sufficiently high temperature in dry air, but by occurring in an aqueous medium the products of the oxidation were hydrated. It is probably the oldest and original theory, and was at once discarded when the fact that liquid water was essential was discovered. Nevertheless, it paved the way for the Acid theory.

Various biologists have drawn attention to organisms which decompose ferrous salts, both mineral and organic, and cause the precipitation of rust. It is not surprising, therefore, that a theory should have been brought forward suggesting that such organisms may be a direct cause of corrosion. It is readily proved, however, that corrosion can occur in media which are unquestionably devoid of organic living matter, and, moreover, no organism has yet been found which lives or feeds upon metallic iron. Even assuming that such did exist, they would necessarily have to bring the iron into solution before they could assimiliate it, and this would probably be effected by some acid secretion. The Acid theory would include any process of this kind. The corrosion of iron is not due to bacteria, nor is it prevented by their elimination. The observations recorded by the biologists are most probably due to the decomposition of organic ferrous salts by the organisms which require the organic radicle for their sustenance. The iron will be set free probably as ferrous hydroxide, and the rust is then produced by the process already described.

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CHAPTER III

FORMS OF CORROSION

If the Ionic or Electro-chemical theory of corrosion, as described in the preceding chapter, be accepted it is then easy to divide all practical cases of corrosion into three types :—

(1) Auto Corrosion.
(2) Contact Corrosion.
(3) Externally Induced Corrosion.

The third type of corrosion is the result of the passage of a current, generated from some external source, through the metal whilst the latter is in contact with an electrolyte. If the current flows in that direction which necessitates the metal acting as anode, then corrosion results. If the current flows in the opposite direction, *i.e.*, from the electrolyte into the metal, the latter receives protection from corrosion which may be complete provided the E.M.F. of the current is sufficiently high. The recognition of this fact has been turned to practical account in the Cumberland system of preventing corrosion, of which more will be said later.

Externally induced corrosion is not so common as the other two types, though its frequency has no doubt increased with the more widespread use of electrical power. Thus, the corrosion of the feet of the standards used to carry the overhead cables for electric trams and trains, may often be largely due to leakage from the power transmission, and cases of corrosion in various units of ships equipment have also been traced to the presence of stray fields and leakages. This type of corrosion is nothing more nor less than simple electrolysis, and the corrosion of the metal is strictly comparable with the corrosion of the metal anodes in ordinary plating processes. In the case of iron and steel embedded in the ground, the metal and the soil act as electrodes and the moisture present is decomposed by the current into hydrogen and oxygen. The latter effects the oxidation or rusting of the metal in place of the atmospheric oxygen, whose rate of diffusion through the soil or clay is often so slow that corrosion, if it were dependent on atmospheric oxygen alone, would be extremely slow.

The most commonly occurring types of corrosion are Auto and Contact corrosion. Auto corrosion is that which occurs when a metal is in contact with an electrolyte but is not at the same time in contact with any other electrical conductor, neither metallic nor non-metallic. In the academic case of chemically pure iron, corrosion would proceed simply by the exertion of the solution pressure of the metal, in conjunction with the presence of hydrogen ions and the oxygen dissolved in the electrolyte, which both depolarises the metal surface and oxidises and precipitates the primary products of solution as ferric hydrate or rust. In practical cases, auto corrosion proceeds by the glavanic action which is set up as a result of the heterogeneous structure of the metal or alloy. No commercial metal exists in which there is perfect homogeneity, there is always some characteristic of structure, some slight degree of segregation or the presence of embedded impurities which is sufficient to impart varying potentials or solution pressures to adjacent areas of the metal surface. For this reason auto electrolysis is set up by which the more electro-positive areas dissolve and, in the case of ferrous material, are eventually precipitated as rust. The pronounced heterogeneity of some alloys, such, for instance, as brass, is no doubt largely responsible for the rapidity with which they frequently corrode, and in the case of iron and iron alloys there is a large volume of evidence to show that heterogeneity, whether induced by structure or segregation, etc., is conducive to accelerated corrosion.

Contact corrosion occurs when the metal is in contact with some other conducting material, which is also immersed either wholly or partially in the electrolyte. If this other conductor is a metal, then the corrosion of the first metal will be either accelerated or retarded, according to the electro-chemical relationship between the two metals. If the second metal is electro-positive to the first, then it will protect the latter at its own expense by itself corroding or dissolving preferentially, but if it be electro-negative to the first metal then the corrosion of this will be accelerated (or the second metal will receive protection at the expense of the first). The practical recognition and application of this may be found in the practice of protecting boilers from corrosion by inserting slabs of the more electro-positive metal zinc and in the protective coatings of zinc which are applied to iron products by various processes. Other conditions being the same, the rate of the contact corrosion of a metal is usually greater than the rate of its auto corrosion. If the second conductor is non-metallic in character, it may generally be assumed to be electro-negative to the metal, and contact between them will therefore result in an accelerated corrosion of the metal.

In both types, auto and contact corrosion, galvanic action is the primary cause of corrosion, each process is one of electrolysis, but in auto corrosion the electrolysis is self-induced by inherent characteristics of the metal, and may therefore be distinguished as auto electrolysis, whilst in contact corrosion the electrolysis is the result of the contact between the metal and some other conductor to which it is electro-positive. Since galvanism, then, is responsible for the majority of corrosion troubles, it may be desirable to discuss this action in more detail.

From what has already been said there will be no difficulty in differentiating between galvanic and electrical action, since the latter always implies an externally generated current. The actions are alike in principle, but their results differ greatly in degree and in character. Electrical action usually tends to induce a more or less uniform corrosion over the entire surface of the metal which comes within its sphere of influence, but galvanic action, by reason of the low E.M.F. of the local currents which are generated, and also because of the fact that it may result from the potential differences between adjacent areas (as in auto corrosion) on the same surface, more frequently results in a selective or preferential corrosion of certain portions of the metal. For instance, an electro-positive area in contact with one of lower potential will dissolve in preference to the latter, and the final result is apparent in "pitting." A good example of this is to be found in the corrosion of brass, in which the condition generally known as "dezincification" is often produced. The nett result in these cases is the removal of the more electro-positive constituent of the alloy, *i.e.*, the zinc, which leaves the copper as a porous and spongy residue.

Galvanic action, whether induced by the characteristics of the corroding metal itself or by contact between dissimilar metals, is caused by differences in electrical potentials, or, in other words, and for our purpose more descriptive words, by differences in solution pressures. If two metals are in contact with each other and with an electrolyte, the one with the higher solution pressure will dissolve, and is said to be electro-positive to the other metal, which has the lower solution pressure and which does not dissolve. If a piece of iron and a piece of copper are placed in contact with each other in dilute sulphuric acid, the iron dissolves and the copper remains unattacked. Replace the copper by zinc and in this case the iron is unattacked whilst the zinc dissolves. The zinc, therefore, is electro-positive to the iron and similarly the iron is electro-positive to the copper, and in the electrolyte the direction of the galvanic current will be respectively from the iron to the copper and from the zinc to the iron, that is, from the more electro-positive metal to the less electro-positive metal. It is clear, then, that the more electro-positive component of such couples functions anodically, and conversely it may be correctly inferred that *whenever a metal functions cathodically it does not corrode.*

Referring again for a moment to externally induced corrosion, these observations give further emphasis to the statement that for an externally generated current to cause corrosion it must flow from the metal into the electrolyte, and that in cases where it flows in the opposite direction its action tends to be, and will be, protective, if its E.M.F. is of sufficient magnitude. Such methods of electrolytic protection as the Cumberland system (*Trans. Faraday Soc.*, **11**, 1915-16) are therefore theoretically sound, as also is the practice of boiler protection with zinc slabs, whereby a protective galvanic current is produced for which the metal of the boiler acts as cathode, receiving the current from the anodic zinc through the water. Unfortunately, however, secondary influences arise in practice which seriously reduce the efficiency of this type of theoretically sound protective measure, in some cases even reversing the intended order of things and thus accelerating corrosion.

The following table gives a list of the commoner metals arranged in order of their solution pressures or electrical potentials. Any metal in the series is electro-negative to all metals which precede it and electro-positive to all which follow it :—

Potassium
Sodium
Barium
Calcium
Magnesium
Chromium
Manganese
Zinc
(Hydrogen)
Aluminium
Iron
Cobalt
Nickel
Lead
Antimony
Bismuth
Arsenic
Copper
Tin
Mercury
Silver

(Iron carbide)
(Iron oxide)

If any two of the above metals are immersed in an electrolyte, either in contact with each other, or kept apart and connected externally instead by a wire, then the one which precedes the other in the series will dissolve or become the anode for the current generated, whilst the one appearing later in the series becomes the cathode and does not enter solution.

For the large majority of cases this may be accepted as the rule, but it must be remembered that the relationship between the solution pressures of two metals may be influenced by other factors such as the concentration, composition, and temperature of the electrolyte. It does not invariably follow, therefore, that, because under one set of conditions a certain metal exhibits a higher solution pressure than a second, this will always be the case. The relationship may be reversed (reversal of polarity), so that the metal which was originally electro-positive is now electro-negative, or the magnitude of the difference between the two solution pressures may be increased or reduced, as evidenced by an accelerated or retarded rate of corrosion or solution of the anodic metal.

This offers some explanation for many curious anomalies which contact with corrosion troubles is sure to present sooner or later, and at once points out the foolishness and futility of attempting to form a generally applicable estimate of the relative corrodibilities of various metals, say of cast iron and steel, for instance. To be of any practical value such comparisons will have to be made for each specific set of conditions, and the choice of either cast iron or of a particular kind of steel must be made, not from a general consideration as to which material is generally regarded as least corrodible, but from a consideration as to which metal has been proved by experience or by definite experiment to be the most suitable for use under those particular conditions to which it will be exposed during service. There have been innumerable assertions by manufacturers of various kinds of ferrous materials as to their excellences in rust-resisting properties, but the laboratory tests or field tests upon which these statements are based vary so widely and represent such a limited range of practical conditions that the intelligent consumer pays but little attention to them nowadays, and chooses his material, as far as possible, from considerations in line with the above.

To continue with the discussion of galvanic action, it has been pointed out that chemical heterogeneity, whether the result of segregation, presence of impurities, or peculiar structure, is conducive to galvanic electrolysis or auto corrosion. It is also known that physical heterogeneity has a like effect. Strained portions of a piece of metal exhibit different potentials to the unstrained portions. Experimental proof of this may readily be obtained by taking a bar of metal, say iron or steel, cutting it into two halves, and then straining one of the pieces in some way, either by tension or torsion, etc. If the two pieces are now placed apart in an electrolyte and connected externally by wires through a galvanometer, it will be seen from the deflection of the latter that a current is flowing, thus demonstrating that the two pieces of metal, originally alike, now have different solution pressures. There is no general rule by which we may predict whether the strained metal will be electro-positive or electro-negative to the unstrained metal, this relationship being largely dependent on other local influences. The modification in the potential produced by straining is always of very small magnitude.

Two characteristic and frequently occurring practical illustrations of the effect of straining a metal are to be found in the rapid corrosion which may be often observed to take place on the metal immediately surrounding the rivet holes which have been punched in steel plates and on the bends on angle irons, etc. In each case the metal in these areas has been subjected to severe strain, and where the conditions are such that the strained metal behaves electro-positively to the general bulk of the metal, these portions corrode more rapidly.

An ingenious and convincing method of demonstrating the galvanic mechanism of auto corrosion was perfected by Cushman and Walker (*J. Amer. Chem. Soc.*, 1907, **25**, 1257, and *J. Iron and Steel Inst.*, 1909, **1**, 33), who introduced the reagent now known as ferroxyl.

When a strip of iron corrodes by auto corrosion there will be, at the positive areas or points, a concentration of ferrous ions, whilst at the negative points, where no solution of the metal occurs, there will be a concentration of hydroxyl ions. If a trace of phenolphthalein is present in the electrolyte it will indicate the electro-negative or cathodic areas by the development of a pink colour, and if, in addition, there is also present a little potassium ferricyanide, this will show up the electro-positive or anodic areas by the production of a blue colour, due to the formation of Turnbull's blue by interreaction between the ferrous ions and the potassium ferricyanide. Cushman and Walker prepared the ferroxyl reagent by stiffening the electrolyte with agar-agar or gelatine, so that it sets to a jelly on cooling. The result is that the colours produced are much more permanent and less affected by external influences.

If a piece of iron is properly mounted in this reagent, the colours which develop are definite proof that the solution pressure of the metal varies at different points on its surface, and that its corrosion proceeds, therefore, by galvanic electrolytic action. Fig. 5 shows three needles mounted in ferroxyl. The strongly-defined blue areas and the somewhat hazy pink areas indicate the non-uniformity of the metal, which was taken direct from the packet in which it was purchased and simply cleaned in aclohol before being mounted. Fig. 6 is a further illustration in which the metallic objects consist of two needles and an ordinary nail. The reproductions of the preparations are not all that could be desired, but the fact that there are three strong colours, the yellow of the ferroxyl mount, the blue, and the pink, does not facilitate faithful photographic reproduction.

The use of this reagent affords also convincing proof of the correctness of the Electro-chemical or Ionic theory of corrosion. The ferroxyl is extremely sensitive and has been of considerable value in the theoretical study of corrosion. It shows very plainly that even the purest iron develops points of different potential in an electrolyte, and that, therefore, perfect homogeneity would appear to be an unattainable ideal. The more pronounced the heterogeneity of the specimen, the stronger are the colours produced, the more clearly defined are their outlines, and the greater is the speed with which they are developed.

A further interesting phenomenon which is clearly evidenced by ferroxyl is the reversal of polarity which may occur between electrodic points on a corroding iron surface. When corrosion first commences the cathodic and anodic areas are indicated by the pink and blue colours as already described. After a time, however, it may sometimes be observed that the originally blue areas are dispersing and are being replaced by pink zones, whilst the pink zones are being replaced by blue ones. The explanation of this is not difficult to find. The continued solution of an anodic area may result in the exposing of an area which is electro-negative to the original cathodic area so that the latter now commences to act anodically. Such reversals in polarity between points on the metal surface may occur frequently, and it is not assuming too much to say that the more homogeneous the metal, the greater the frequency of reversal, and hence the more uniform the corrosion. Conversely, the more pronounced the segregation or heterogeneity, the greater the tendency to corrosion in the form of pitting.

Whilst the ferroxyl reagent is of undoubted value in demonstrating the electro-chemical mechanism of the corrosion of iron and the effects which segregation and local strain tend to produce, or induce, yet it would not appear to be a warrantable procedure to apply unreservedly the inferences from observations of the behaviours of metals in the reagent to actual practice. In the first place, corrosion in the reagent takes place under unique and highly specialised conditions (conditions which would never obtain in practice) which remain comparatively constant and which are but little affected by external influences. The conditions under which metal corrodes whilst in service are infinitely more complex and are constantly being aggravated or alleviated, added to, or reduced in number. The anodic portions of specimens mounted in ferroxyl may be proved to coincide with known variations in the nature of the material, such as the presence of impurity, segregation or strain, and though it may be correctly inferred that such variations facilitate electro-chemical action, it does not necessarily follow, for instance, that a strained portion of a piece of metal will act anodically in service. The reagent is so designed that it is very sensitive to extremely slight differences in electrical potentials, the effects of which may readily be masked, reversed, or rendered negligible in the presence of other corrosive factors which occur in practice.

PASSIVITY

The recognition of the "passive" or chemically inactive state of iron is one of long standing, but up to the present time no theory has been advanced which gives a thoroughly satisfactorily or complete explanation of the phenomenon. It is beyond doubt that passivity, however induced, is wholly associated with the surface film or layer of the metal, and the behaviour of passive iron may be due equally well to either a physical or a chemical change in this layer. Many instances might be quoted to illustrate the varying degrees of chemical activity which may be conferred upon a substance by alterations in its physical condition, the chemical composition and structure remaining, withal, unchanged.

A strict criticism of what is implied by the term "passive," *i.e.*, chemical inactivity of the **Metal**, would necessitate its interpretation as a definite or peculiar physical condition; for if passivity is the result of a change in the chemical condition, such, for instance, as the deposition of an oxide or gaseous film, then the activity of the underlying metal is obviously unimpaired, but is prevented from manifesting itself by the presence of a protective film or coating whose extremely low solution pressure renders it more or less permanent. Hence if passivity is due to such a protective film on the metal surface, the term cannot be rightly regarded as denoting a specific condition or property of the metal.

As generally understood, however, "passive" is the term used to indicate that *condition of the metal in which the appearance of its surface is not visibly altered, but in which its chemical activity or solution pressure is reduced almost to nil.* The condition is always fugitive, though the length of its duration may vary according to the method by which it is induced, and it is considerably lengthened if the passified iron is kept dry (Heathcote, *J. Soc. Chem. Ind.*, 1907, **26**, 899).

It is usual, for purposes of demonstration, to passify iron by immersion in strong nitric acid, and it was in this manner that the phenomenon was originally observed. It was soon found, however, that other acids, such as chromic, iodic, and chloric acids, would induce the same condition as well as mixtures of acids and salts, or even aqueous solutions of certain salts, for instance, lead and silver nitrates, permanganate, and bichromate of potassium, provided suitable concentrations were employed. Passivity may also be induced by momentarily heating the metal in air or by exposure to certain gases, such as nitric oxide and nitric acid fumes. Iron may also be rendered passive by making it the anode during the electrolysis of an aqueous electrolyte, usually caustic soda.

The outstanding property of passive iron is, of course, its reluctance to enter into those reactions which characterise the active metal. It will not rust, for instance, and it is insoluble in acids, unless made the anode for an electrolysing current. Its rust-resisting properties have naturally attracted attention with a view to producing a permanently passive condition, but so far without success, so that the passive condition cannot yet be turned directly to any practical account, though certain passifying agents are of considerable importance in the protection of iron and steel. The other properties are only of significance in illustrating the methods by which passivity may be destroyed, etc., and in providing evidence either for or against the several theories which have been suggested to explain the nature of the passive condition.

The oldest theory is, strange to say, the one which has proved to be the most compatible with the facts which subsequent research has brought to light, and is therefore the one which has received the most generous adoption. That it is not wholly beyond criticism will soon become apparent, and although it is the generally accepted explanation, yet it is felt that an entirely satisfactory theory has still to be evolved.

The Oxide theory assumes that passivity is the result of the production of a film of metallic oxide, which covers the entire surface of the metal and prevents it from coming into contact with reagents to whose attack it is susceptible. The film may—must, in fact—be so thin that it is impossible to detect its presence even microscopically. An iron mirror may be rendered passive without incurring any estimable reduction in its reflecting power. Provided it is continuous and unbroken, the film may be so tenuous that its thickness may be regarded as being of molecular dimensions. Its composition has been the cause of much speculation, and although several alternatives have been suggested it is generally considered to consist of ferroso-ferric oxide, Fe_3O_4.

A second theory attributes passivity to the formation of an adherent film of gas which acts similarly to the film of metallic oxide discussed above. The gas may vary in kind according to the method used in passifying: thus it has been suggested that passivity induced by anodic polarisation in sulphuric acid is the result of a film of gaseous oxygen, whilst passivity produced by immersion in strong nitric acid is due to an oxide of nitrogen film. This is known as the Gaseous Film theory.

The third, or Physical theory, presumes an alteration in the physical or electrical condition of the surface of the metal by passifying agents, such as the production of trivalent iron. How far this assumption is justified it is difficult to say, there is no evidence to show that trivalent iron is inactive chemically; this is certainly not the case when trivalent iron occurs in combination with other elements. If, however, passivity is really a metallic property and not the result of protection as assumed by the Oxide and Gaseous Film theories, then the Physical theory would appear to be the most rational, but since we do not know whether passivity is a metallic property or not, this theory must be accepted or rejected on its merits as revealed by a careful examination of the evidence available. Since, however, the passivities produced by alternative methods are not in every case identical in their behaviours, it may be possible that each theory is applicable to certain forms of passivity.

The evidence from which an estimate of the comparative validities of these theories may be formed may be summarised in the following manner by considering some well-established properties of passive iron. When passivity results from immersion in a liquid media the latter is invariably an oxidising agent. This provides considerable evidence in favour of the Oxide theory, but it does not necessarily reflect adversely on the other two theories. The gaseous oxygen which may be liberated on the surface of the metal would conform to the Gaseous Film theory, since this oxygen need not combine with the iron. It is known that the metal may remain in contact with oxygen, under certain conditions, for an indefinite period without any combination occurring between the two elements. We are also bound to regard the film of gas as sufficiently continuous and impenetrable to prevent contact between the iron and the liquid medium, and in the absence of such contact reaction between the metal and the oxygen will not take place. Again, contact with an oxidising liquid may be looked upon as particularly favourable to the production of a physical change in the metal, such as the formation of trivalent iron or other modification in the electrical condition of the metal.

Passive iron is readily restored to its original active condition by various chemical and mechanical means. Immersion in dilute acids destroys passivity, and the rate of destruction is accelerated by those external influences, such as elevation of temperature and mechanical agitation, which usually increase the rates of chemical reactions. Lightly scratching the surface, or rubbing, renders passive metal active, as does also the galvanic effect produced by contact, whilst in an electrolyte, with a piece of a more electro-positive metal, *i.e.*, zinc. These observations lend support to the Oxide theory and also to the Gaseous film theory. The action of dilute acids and the acceleration of this action by the agencies referred to may be explained by the fact that the tenuous film of iron oxide is dissolved by the acids, or that the hydrogen liberated on the iron, when the latter is acting cathodically in contact with zinc, reduces the oxide film or the gaseous oxygen film, thus removing the cause of passivity, whichever this may be. Mechanical abrasion would, of course, destroy either form of protection, if not wholly, by at least so damaging it that its continuity is broken, thereby exposing the electro-positive metal beneath it to attack, when such action will be accelerated by differences in potential between the remaining portions of the film and the exposed metal. The remainder of a film of such excessive thinness as is assumed to suffice to impart passivity would, under these conditions, be almost instantaneously removed, and hence the apparent result that scratching, etc., renders all portions of the surface active simultaneously. It has been shown, however, that the untouched areas are not actified in this way. If a piece of passive iron is scratched at one end then the immersion of the other end in some reagent shows that it is still passive, but if the level of the liquid is raised until the damaged end is submerged, then the whole piece at once exhibits activity.

It has already been pointed out that passivity is fugitive, and this fact has been quoted as evidence against the Oxide theory. Such evidence is not conclusive, however; it is clear that moist conditions will accelerate the activation of passive iron, but even in the absence of moisture an oxide film of molecular dimensions as regards thickness may be anticipated to be extremely susceptible to such influences as slight variations in temperature, etc., which could result in the flaking off of the film in much the same way as hammer scale is known to peel away from iron articles.

Another method by which passivity may be destroyed is by heating the passive metal in a reducing atmosphere, and this may obviously be acclaimed as substantial evidence in favour of the Oxide and Gaseous Film theories, for in a reducing atmosphere it is equally easy to imagine the reduction of either a metallic oxide film, a gaseous oxygen film, or a gaseous oxide of nitrogen film. Galvanic activation may be explained in the same way, since when the passive iron is made cathodic, gaseous hydrogen will be liberated on its surface and may reduce the passivifying film as above. This process of destroying passivity does not appear to afford much support to the physical theory, except that it might be argued that if an oxidising medium is conducive to the production of that physical condition which confers passivity on the metal, then the antithesis of this, *i.e.*, a reducing medium, may be expected to operate in the reverse direction, by restoring a normal physical condition associated with normal chemical activity.

Heathcote (*J. Soc. Chem. Ind.*, 1907, **26**, 899) threw considerable doubt on the tenability of the Gaseous Film theory by carefully conducted experiments, in which he showed that, contrary to previously recorded observations, passivity is not destroyed by high *vacua*. In his experiments the passive material was subjected to pressures of the order of 1/50 of a millimetre, and it is only reasonable to suppose that any film of gas on the surface of the metal would have been broken up by such treatment, especially as it was observed that the metal gave up occluded gases. Yet on removal from the apparatus the iron was still passive.

Further observations might be given to supplement the foregoing, but they would serve no further purpose than to emphasise that the cause of passivity has still to be definitely established, though it may ultimately be found that each theory is correct in that passivity may not necessarily be the result of one particular cause only, but may be induced by a number of alternative causes.

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PART II

THE CAUSES OF CORROSION

CHAPTER IV

THE FUNCTION OF OXYGEN

THE records of observations on practical cases of corrosion are very conflicting, and it would appear at first sight that iron and steel behave very erratically when exposed to corrosive influences. Common sense, however, precludes this view, since in other directions a constancy of behaviour is readily seen to be exhibited.

If a series of experiments is carefully conducted, under identical conditions, on the rates of corrosion of pieces of equal size and shape of a particular sample of metal, concordant results will be obtained, and the reason why such results are the exception in practice is to be found in the fact that, even in the simplest cases, corrosion becomes a very complicated process. It is so greatly and diversely influenced by numerous factors, both external to the field of corrosion and internal to it, that is, directly affecting the metal or the electrolyte. The effect of a single factor, acting alone, may not be difficult to determine, but when several of these factors are acting in conjunction, as is almost invariably the case, it is a very different matter to form an estimate of their nett effect.

The corrosion even of pure iron in pure water and pure air is, under practical conditions, a sufficiently complex problem, but the technical problem is rendered infinitely more so by the fact that pure iron, air, and water are never encountered, and the impurities present in any of them are responsible for further variations in behaviour during the processes of corrosion.

The many factors which influence the rates of corrosion may be classified in two ways :—

1. (*a*) Stimulative factors.
   (*b*) Inhibitive factors.

2. (*a*) Factors which determine the concentration of oxygen in the liquid medium and its maintenance.
   (*b*) Factors characterising the composition of the electrolyte.
   (*c*) Factors inherent in the metal itself and resulting from manufacture or subsequent treatment and sphere of service.

Classification 1 is, of course, a very general one, and the second alternative is perhaps the better for the purpose of a systematic consideration of these variables.

The discussion of groups (*a*), (*b*), and (*c*) in classification 2 will therefore form the subject matter for this and the two succeeding chapters, though it should be remembered that a certain amount of overlapping between these groups is scarcely avoidable, and such factors as temperature, etc., will be dealt with at points where their inclusion appears to be most convenient.

Group (*a*) may be well introduced by an outline of the effects of air and water on iron. By air is here implied the normal atmosphere, unpolluted by industrial gases, and for the present water must be regarded as naturally pure, that is, free from pollution and from the presence of electrolytes. Air and water are both essential to corrosion; neither, in the absence of the other, has any action on iron under normal conditions. Oxidation of the metal in dry air can, of course, be brought about by suitably increasing the temperature, but the process is not one of corrosion. It results simply in the production of a uniformly distributed skin of magnetic oxide of iron, which, unlike the products of corrosion, does not accelerate subsequent oxidation, but retards it by preventing its penetration beyond a thin superficial layer. The colours imparted to the metal surface by this oxide skin are well known and may range from pale yellow to black, according to the temperature employed. The gradually deepening colours correspond to increasing thicknesses of the coating, and although this is primarily a function of the temperature, the duration of the period of exposure to the heat has also an appreciable effect.

The action of pure water alone on iron has already been shown to have been the subject of much research and controversy. For all practical purposes, however, it may be looked upon as *nil*, for even though the metal be soluble in it to a slight extent, the water would soon become saturated with ferrous ions, and, in the absence of air or oxygen, the state of equilibrium thus reached would not be disturbed and further solution of the metal could not therefore take place.

The same argument holds equally good in the case of natural water containing dissolved atmospheric gases. The oxygen present can only combine with a limited quantity of iron, and once it has done this the above state of equilibrium will obtain and check corrosion. It is clear, therefore, that, for corrosion to proceed, a continual supply of oxygen is necessary, and it follows also that the rate at which the gas can replace that which has already entered into chemical combination with the iron will determine the rate at which the metal corrodes.

In short, oxygen may be regarded as the prime factor in corrosion.

The gas is also equally essential in cases where iron corrodes in slightly acid electrolytes. Under these conditions, the metal goes into solution as a ferrous salt and the acidity will soon be neutralised. The action of oxygen is to decompose these ferrous salts, thereby precipitating ferric hydroxide or rust and liberating the acid, which can now proceed to attack more iron.

The results of the combined action of air and water on iron are common knowledge, and the mechanism of this action has already been discussed. The point which requires emphasis here is that the water must be in liquid form and in contact with the metal (*i.e.*, it must " wet " the metal) before corrosion can proceed, or even be initiated. Moist air has no action on iron, and the latter will remain untarnished and unaffected for an indefinite period in such an atmosphere, provided the metal is constantly maintained at a temperature just above the dew point. Once it falls below this point water will begin to condense in liquid form upon the iron, and corrosion will commence and proceed.

The same remarks may be extended to include an atmosphere of steam. At high temperatures the effect of steam on iron is comparable with that of dry air under similar thermal conditions. A skin of magnetic oxide is formed on the metal by the decomposition of the steam, during which free hydrogen is also produced. But neither is this process one of corrosion as we defined the term in Chapter I. Contact with steam results in corrosion only when the steam is wet and the "wetness" comes into direct contact with the metal. In turbines operating on superheated steam, for instance, the blades of the high-pressure stages do not suffer from corrosion, but become covered with an adherent coating of magnetic oxide, produced by the action of the dry superheated steam, and which, incidentally, protects them from corrosion during shut-down periods. Corrosion of the blades commences at the point where the steam has lost its superheat and is becoming wet. Similarly, the corrosion of steel superheater tubes is generally confined to the inlet or "wet" end, and does not extend along the tubes beyond the point at which the steam becomes dry.

The action of dry steam upon iron and steel is of special interest in that it provides a method of applying protection from corrosion, and a few further remarks in reference to it may be conveniently included at this point.

The reaction is a reversible one and is usually expressed symbolically as follows :—

$$(24)\ 3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

In a closed system, that is one in which there is not a continuous current of steam to sweep away the hydrogen produced, a condition of equilibrium is reached between the iron and the steam and the products of their reaction, namely, magnetic or ferroso-ferric oxide and hydrogen. The quantity of hydrogen produced, as evidenced by its partial pressure, has a definite value for each particular temperature, and this value decreases with increase in the latter variable. The removal of the hydrogen results in the decomposition of more steam and the production of more magnetic oxide, thus increasing the thickness of the skin. If, on the other hand, the partial pressure of the gas is artificially increased by injecting more of it into the system, the reaction (24) proceeds towards the left until equilibrium is restored, that is, some magnetic oxide is reduced by the excess of hydrogen yielding steam and metallic iron.

Friend attempted to determine the minimum temperature at which steam begins to attack iron, or rather at which iron begins to decompose steam, and as a result of his investigations, found that at 350° C. the action is such as to produce a visible effect after one hour's exposure. He concludes, therefore, that the action must commence at temperatures below this but that it is not possible to fix a minimum limit to the temperature, since the action would then be so slow that a long period would be required before its results became visible.

To continue now with the combined action of air and water, it is necessary to examine those factors by which the rate of the supply of the prime factor, oxygen, to the vicinity of the corroding metal is governed, for, as pointed out above, although the solution of iron in water may commence independently of oxygen, the continuation of the process and its rapidity is entirely dependent upon a continuous and adequate supply of this gas.

Most of us will doubtless have observed that, in the case of iron railings, rapid corrosion occurs at the point where they enter the ground. They may frequently be found to be corroded completely through at this point, whereas above it their condition is as good as new, whilst the portions below the ground surface may also be in a reasonable state of preservation. This commonly occurring example illustrates very forcibly the way in which the rate of corrosion is accelerated by a ready access of oxygen to its seat. The bottoms of the rails, about which moisture drains and collects, obtain a maximum supply of water plus oxygen; their upper portions soon shed any rain, etc., and residual moisture is quickly evaporated, with the result that they are attacked only in a comparatively slight degree. The ends of the rails embedded in the ground, although perhaps continually in contact with moisture, also suffer less from corrosion, because the supply of oxygen, necessary to the maintenance of the rusting process, is determined by the speed at which the gas can diffuse through the ground. This speed will, of course, vary considerably in different localities, but the supply of oxygen to the metal will clearly be always more slowly maintained than is the case on and above the ground level.

As a general rule, and unless the ground has some peculiar characteristic, such as acidity, the corrosion of embedded iron becomes less rapid the deeper it is buried. In certain cases, however, the soil itself may be corrosive, it may contain salts, such as magnesium sulphate, which are known to be corrosive, or a combination of salts which, though they may be harmless individually, yet when occurring together impart an acid reaction to the soil. Carbonate of lime, for example, is a common constituent of soils, and alone would tend to hydrolyse and confer a slight alkalinity on the soil. In the presence of carbon dioxide (carbonic acid) this tendency is suppressed, and the soil is likely to become slightly acid. The products in equilibrium in the soil are, expressed in ionic terms :—

$$(25)\quad \begin{array}{l} (a)\ \mathrm{Ca}^{\cdot\cdot}\cdot\mathrm{CO}_3'' = K \\ (b)\ \mathrm{H}^{\cdot}\mathrm{H}^{\cdot}\cdot\mathrm{CO}_3'' = K \end{array}$$

If calcium sulphate is also present, a third pair of products must be taken into account :—

$$(26)\quad (c)\ \mathrm{Ca}^{\cdot\cdot}\cdot\mathrm{SO}_4'' = K$$

The calcium content of the solution is increased by the presence of the calcium sulphate and the CO_3'' content proportionately reduced. The equilibrium expressed in (*b*) is disturbed in consequence, and in order that the constant K may be satisfied, when CO_3'' is reduced the $H^{\cdot}H^{\cdot}$ must increase by a proportionate amount. The result therefore of the combined presence of sulphate and carbonate of lime is to increase the acidity of the soil.

The significance of a number of factors may be readily appreciated by considering their influences as affecting the supply of oxygen to the seat of corrosion.

In the case of iron immersed in a continuous stream of rain water, for instance, in the upper reaches of rivers, we should anticipate most rapid corrosion. Rain water is generally almost saturated with atmospheric oxygen, and the flow of the river maintains a continuous contact between the metal and the fully oxygenated water, ideal conditions for violent corrosion. The strongly corrosive action of rain water, which is practically pure as regards dissolved solids, is now generally recognised, and the absence of soluble salts, whilst very desirable from many points of view, is to some extent responsible for this. Their presence would tend to lower the solubility of oxygen in the water, and the quantity of the active gas might also be further reduced by its absorption or combination with the dissolved impurities, notably those of an organic character.

Waters which are exceptionally free from dissolved solids very often cause serious corrosion when used industrially, as for steam-raising, etc., and this is due entirely to the large quantity of dissolved oxygen which they contain. The elimination of this dissolved gas is a problem to which considerable attention has been paid during the past few years, and as a result the subject of water-treatment has expanded to include processes having this object in view.

In the majority of cases, therefore, the quantity of oxygen present in the water is a factor of primary and paramount importance.

The rate of flow of the water over the corroding surface has also a direct influence on the rate of corrosion, more pronounced in deep waters than in shallow ones, since in the latter the atmospheric oxygen has a less depth of liquid through which to diffuse, and consequently the rate of flow of the water is not so vital in such cases. In deep waters, however, unless the flow be fairly rapid, the zone of deoxygenated water which is produced about the metal by its corrosion will be replaced but slowly, particularly the layer or film immediately in contact with the metal, whose removal is rendered somewhat more difficult by the friction existing between it and the metal surface. If this surface is already covered with a layer of rust, then this film of water is still more tenacious, since it is entangled, so to speak, in the porous structure of the corrosion products. Similar considerations apply to the corrosion of the interior surfaces of water pipes, the amount of corrosion being largely determined by the rate of flow, or quantity of water passing through them. In cases of this kind atmospheric oxygen is, of course, completely excluded, and corrosion is dependent for its progress upon the oxygen which is conveyed in the water in solution.

In the case of metal standing in running water, then, the rate of its corrosion is determined by the volume of water which passes over its surface, simply because the rate of flow of the water determines the rate of the supply of oxygen to the corroding metal, and, other conditions being the same, the rate of corrosion is directly proportional to this. Exceptional cases may be met with in which the velocity of the water is very high, and under these conditions corrosion may be retarded or even completely arrested, as explained in Chapter II., where Friend's Colloid theory of corrosion was dealt with.

Turbulency and violent agitation of the water have an effect comparable with rapid flow, since they help to maintain a fresh supply of water to the metal surface, and, in addition, will also tend to maintain a high and constant oxygen content in the water by aëration.

When iron rusts in stagnant water other influences come into play. If we consider the case of an iron column or pillar which stands in a pool or lake, it is clear that its corrosion will be most severe on the air-water line, for at this point the supply of oxygen is most easily maintained and the concentration of the gas will be highest. The gas has but a thin surface film of water to penetrate in order to reach the seat of corrosion. Proceeding downwards along the submerged portion of the pillar, this penetration or diffusion is rendered increasingly more difficult and in consequence, slower. A proportionate falling off in the rate of corrosion occurs, therefore.

The depth of immersion of a metal has, then, a marked effect on the rate of its corrosion and, in addition, on the retarding action resultant from the above considerations. It also operates in the latter direction by reducing the intensity of light which reaches the corroding metal. It is well known that the velocity of many chemical reactions is considerably increased by increasing the intensity of the light under which they are progressing, and, as has been demonstrated experimentally by Friend and others, the rusting of iron forms no exception to this general rule. The further we proceed below the surface of the water the more feeble the light becomes. Increasing the depth of immersion results in a shuttering-off of an accelerating influence.

Examples in which the combined action of the factors so far dealt with is operative may be found in closed iron tanks, deep wells, and pipe lines through which the flow of water is slow or intermittent. In each case the access of atmospheric oxygen is rendered more or less impossible, and the water, and any air which may exist above its surface, are soon deprived of their oxygen, and this is not replaced until, in the case of pipe lines, the flow of water is recommenced, or in the case of tanks and wells, the stagnant and devitiated air is changed.

Another feature which will obviously affect the rate or amount of oxygen which can diffuse through the water is the area of the exposed surface of the latter. The larger this area, the greater the quantity of oxygen which can pass into solution in a given time to replace that used up in the process of corrosion. In this connection the volume of water is of minor importance, but the restriction of its surface area is equivalent to reducing the rate of the supply of the prime factor. In fact, it is easy to conceive that if its exposed surface is restricted, the larger the volume of the water the less rapid will be the rate of corrosion, for if its surface area is small, the concentration of oxygen maintained in the water will also tend to be of low magnitude. Friend has demonstrated the influence of surface area in a simple manner by taking a number of glass dishes of uniform circular sections and placing in each a piece of pure iron foil and covering the metal with an equal volume of water in each case. On the surface of the water he then floated wax discs, cut to fit the dishes. In the centre of each disc was cut a hole the diameter of which was varied in different discs. In this way varying areas of water were exposed to the atmosphere whilst other conditions remained unchanged. The relative rates of corrosion of the pieces

of iron, as indicated by observations in loss of weight, are reproduced in the following table and illustrate very effectively the marked influence which the area of the exposed surface of the water may have on the rate of corrosion of metal immersed in it.

Area of exposed surface of water.	Original weight of iron.	Loss in weight.	Relative corrosion.
56·8 sq. cm.	7·9490 grm.	0·0382 grm.	100
12·6 ,, ,,	7·9100 ,,	0·0220 ,,	58
0·8 ,, ,,	7·8926 ,,	0·0052 ,,	14

The effects of increase in temperature on the rate of corrosion of pure iron in pure water are two-fold and opposed. In the first place, it exerts its customary effect by increasing the rate of corrosion, or chemical action. At the same time, however, the solubility of oxygen in water decreases with rise in temperature, and a reduction in the rate of corrosion is thereby occasioned. At the boiling point the solubility of oxygen in water is *nil*, and at this temperature corrosion cannot therefore proceed. It follows, then, that there must be some particular temperature at which the combined influences of heat and reduction in the quantity or concentration of oxygen available will have a maximum value, and at which corrosion will proceed at a maximum rate. Exactly at what temperature this occurs does not appear to have been finally settled, the figures quoted by different workers involving a range of about 20°, *i.e.*, from 60 to 80° C.

In practical cases, rise in temperature is directly responsible for accentuating the effects of other factors, and also for bringing into action factors which are normally inert or negligible. Thus galvanic action, no matter what causes institute it, is considerably facilitated by an increase in temperature, and in some cases may even be initiated in this way by unequal heating of the corroding metal, differences of potential being exhibited between the hotter and cooler portions. When commercial iron or steel corrodes, there occurs a slow oxidation of the sulphur and phosphorus contents, producing acids which, of course, accelerate corrosion. Elevation of temperature will speed up this production of acids and at the same time enhance their solvent action on the metal. When exceptionally high temperatures are employed, as, for example, in boilers, decomposition or hydrolysis of the solid constituents of the feed-water may occur in which the acid radicles are liberated and may carry on the corrosion of the boiler plates and tubes independently of any atmospheric oxygen.

The attack under these conditions is frequently very severe. The chlorides and nitrates of the alkaline-earth metals are the principal offenders in this direction. The nitrates, being powerful oxidisers, may be regarded as supplying the oxygen necessary, whilst the chlorides, acting catalytically, result in oxygen being supplied by the water itself.

The effect of variations in temperature on the conductivities of solid and liquid conductors, *i.e.*, the metal and the electrolyte, will doubtless have also an appreciable influence on the rate of corrosion.

Other factors which, acting indirectly by their influence on the rate of supply of oxygen and its quantity, will no doubt suggest themselves to the reader, but sufficient has been said to illustrate how considerably these may affect the rates of corrosion under varying conditions. The physical treatment and condition of the metal cannot be disregarded as sources to which other accelerating and inhibiting factors owe their origin, but oxygen should be looked upon as the predominating factor, which during the first stages of corrosion can obscure influences arising from the composition and condition of the metal, and which is chiefly responsible for determining the subsequent rate of corrosion, both directly and also indirectly by acting through the corrosion products.

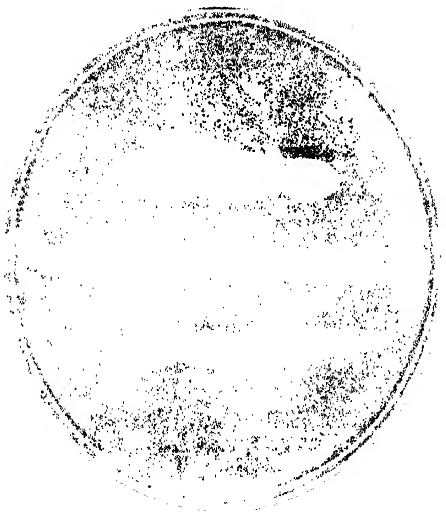

FIG. 5.—STEEL NEEDLES MOUNTED IN FERROXYL.

The production of rust is to most people the result and chief characteristic of ordinary cases of corrosion, but it is not always realised to be an accelerating factor, which may have a most pronounced influence on the rate of corrosion proceeding in its presence.

The structure and composition of rust varies very considerably according to the conditions prevalent during its formation. In most cases the final product is hydrated ferric oxide, the extent of hydration being again determined by the local conditions. The product immediately in contact with the metal is usually ferrous hydroxide, and may often be seen by detaching the pieces or flakes of rust from corroding iron and examining their under surfaces. Ferrous carbonate is also a frequent constituent, and, in addition, ferroso-ferric oxide or magnetic oxide, produced by a partial reduction of ferric oxide, is often present. The proportion of ferrous oxide in rust varies between very wide limits; in cases where the supply of oxygen has been inadequate or almost entirely withheld, the percentage of ferrous oxide reaches a very high figure, whilst in others, in which oxygen has had unrestricted access, its amount may be barely sufficient for its detection.

One reason why corrosion is accelerated by the presence of rust is to be found in the fact that metallic oxides are electro-negative to their respective metals. Consequently when iron is in contact with its oxide in an electrolyte the latter acts cathodically and speeds up the solution of the metal. Further, this oxide can also act as a depolariser, and the presence of magnetic oxide in rust may be attributed to this action, which would proceed as follows:—

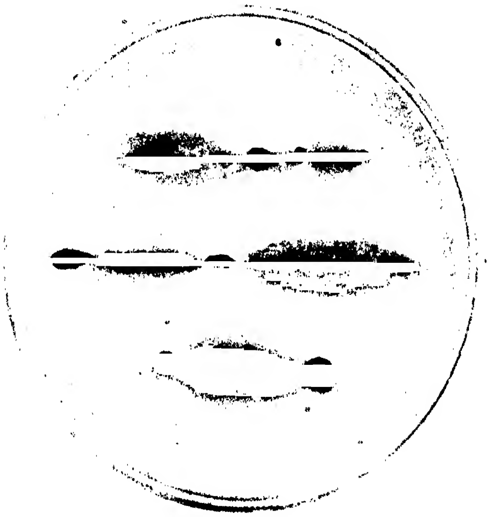

FIG. 6.—STEEL NAIL AND NEEDLES MOUNTED IN FERROXYL.

$$(27)\quad 3Fe_2O_3(\text{rust}) + H_2 = 2Fe_3O_4(\text{magnetic oxide}) + H_2O$$

The porous nature of the rust and the fact that it is hygroscopic also result in the absorption of atmospheric oxygen and moisture on its surface, and this adds further to its activity as an accelerating or stimulative factor.

The physical condition of the rust formed plays an important part in the subsequent progress of corrosion. Its formation is dependent upon the presence of water and atmospheric oxygen, but the conditions under which the metal is attacked are responsible for the physical characteristics assumed by the products. Under certain conditions, the rust may be hard and dry and firmly adherent to the metal; at other times it may be wet and spongy and readily detachable. The latter variety will naturally induce accelerated corrosion, whilst the former may have a tendency to operate in the opposite direction, that is, to retard corrosion, though cases in which the products actually afford protection to the underlying metal, whilst not inconceivable, are rarely, if ever, encountered. The harder the rust, the more readily does it tend to flake or scale off and expose a fresh metal surface, either wholly or in patches of greater or lesser area. The partial removal in this way of a hard dry rust, brought about by temperature fluctuations, mechanical stresses, and general alternations in the local conditions, will considerably accelerate the corrosion of the exposed metal, and if the exposed patches are individually of small area, pitting will occur. Corrosion which originally may have been more or less uniform can thus be altered in type directly through the behaviour of the products, which is, in turn, determined by their physical condition.

The transportation of rust particles by moving water can cause deep pitting on other iron surfaces on to which they are swept by the current. Their action in such cases is, of course, primarily electrolytic.

It may be of interest in this connection to consider briefly the mechanism whereby this characteristic form of corrosion, known as pitting, is produced, and also of the formation of rust cones, the explanation of whose production is closely allied to that of pitting.

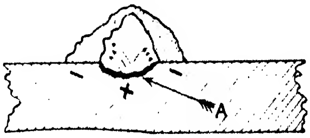

FIG. 7.—THE FORMATION OF RUST CONES AND PITS.

If we consider the corrosion of a bar of iron which is quite uniform, both chemically and physically except for a small spot, *A* (fig. 7), which we will assume to be electro-positive to the bar as a whole, and whose presence may be due to some peculiarity of structure, etc., then, as corrosion proceeds, the material at *A* will be preferentially dissolved, since it has a higher potential than the rest of the metal. The depth of the pit thus produced will depend upon the depth of or extent of the electro-positive portion, *A*, and the pitting will cease to penetrate further when the uniform metal is reached. The same process goes on if *A* is replaced by a particle of some electro-negative body, for instance, a fragment of rust or coke, etc. A galvanic couple will be set up between this and the metal in the immediate vicinity of the point of contact, and a pit will be formed as a result of the solution of the electro-positive iron. Small particles of coke and other electro-negative bodies have been held to be responsible for the extensive pitting which sometimes occurs on brass condenser tubes, and the actions in each case are comparable.

Referring again to fig. 7, the ferrous ions resulting from the solution at *A* will exist as colloidal ferrous hydroxide and, as positive colloides, will migrate to the negative pole of the galvanic circuit, namely, the circle of metal surrounding *A*.

Here they will be precipitated as ferric hydroxide by the oxygen dissolved in the water and, as corrosion proceeds, a wall of this material will be built up around the electro-positive area. This wall may continue to grow inwards until a dome or cone is formed, or, if the depth of water over the surface of the metal is very slight, the walls may be roofed in prematurely by a skin consisting of colloidal ferric hydroxide as soon as they reach the surface. It must be borne in mind that fig. 7 is very much exaggerated, and that in practice the cones are formed almost before they are sufficiently large for their characteristic appearance to be recognised. Their growth takes place from the inside. Skins of precipitated colloidal ferrous hydroxide may frequently be observed on the still surfaces of water in which iron is corroding under particularly uniform and undisturbed conditions.

Another process of cone formation may occur as follows:—if we reverse the conditions in fig. 7, that is, assume the patch *A* to be electro-negative, then ferric hydroxide will be precipitated and piled up on the surface of *A* as the electro-positive metal surrounding it corrodes.

The initiation of corrosion on a polished iron surface is much more difficult than it is on an unpolished surface of the same material, but once corrosion has commenced it proceeds at a rate out of all proportion to its speed of initiation. The presence of rust may be reasonably held to be responsible for this, and although it may be argued that, as the highly polished surface becomes roughened by the attack the subsequent corrosion is accelerated or stimulated by the porosity of the metal which the original polish more or less effectively masked, yet very little practical observation is required to impress the fact that once iron or steel begins to corrode under conditions which permit the products of its corrosion to remain in contact with it, the process becomes one of extreme rapidity, and, further, no matter what steps are taken to arrest the corrosion, these will meet with but indifferent success so long as any rust remains in contact with the metal.

It was stated earlier in the chapter that iron could be preserved indefinitely in a damp atmosphere without corrosion occurring, provided its temperature was maintained constantly above the dew point. If the products of corrosion are already present on its surface, however, this statement must be modified. Rust is hygroscopic, and can therefore absorb atmospheric moisture and in this way assist the process of corrosion under these conditions.

Oxygen, then, must be considered, not only as an essential factor to corrosion, but also as the one which is primarily responsible for the progress and rate of corrosion. Only in exceptional cases do other factors assume or attain more than a secondary importance, but of these, the ones which have a direct influence on the supply of oxygen take precedence, and rust may be regarded as being well towards the top of this list.

The atmosphere normally contains carbon dioxide to the extent of from 2·9 to 3·0 cubic centimetres per 10,000 of air. The gas is very soluble in water and forms in solution the weak acid, carbonic acid. This was originally looked upon as the chief cause of corrosion, and although such conceptions have been greatly modified, it still retains its reputation as a very active factor whose accelerating influence is readily detectable if its quantity slightly exceeds the normal. Concerning the effects of other atmospheric constituents, such as occur in the air of towns and industrial centres, little need be said beyond indicating their composition and the extent to which they occur, since their effect on corrosion may readily be anticipated from their nature. Chief amongst them are the compounds of sulphur, the dioxide, the trioxide (sulphuric acid), and the sulphide. Each of these confer acidity on rain water, etc., and thus add their quota of stimulative influence. The amount of these sulphur compounds, estimated as sulphuric anhydride, normally present in the air of large towns is about 1·5 to 2·0 cubic centimetres per cubic metre, though these figures may be considerably exceeded in certain localities in which the conditions are abnormal. It has also been recorded that common salt, to the extent of about 36 lb. per acre, is annually carried down to the earth by rain, and other salts, such as ammonium nitrate, sulphate, and chloride, may often be detected in rain water. Very dilute salt solutions have a pronounced stimulative action on corrosion processes, and the presence of these salts must not therefore be overlooked as contributory, if minor, corrosive influences.

The Effect of Oils on Corrosion.—The influence of oils on the corrosion of iron may be conveniently included in this chapter, since their action, which is normally a protective one, is due to the exclusion of one or both of the two essential factors to corrosion, water and oxygen. Lubricating oil, for example, prevents the access of moisture to the metal surface, and even though oxygen can diffuse through the oil, as it does through water, corrosion will be prevented. The so-called "drying-oils," used in the manufacture of paint, act in a similar manner. They absorb and combine with oxygen to produce a tough, dry skin which is an excellent water-shedder and may also be a reasonably efficient oxygen excluder.

The direct action of all pure oils on iron may be regarded as *nil*, they have no solvent action on the metal, or at the most this action is so slight as to be of no practical significance. Certain kinds of oils and greases, however, are so constituted that they develop, under favourable conditions, characteristics which enable them to attack iron directly. These are the animal and vegetable oils, which consist of glycerides of fatty acids, that is, compounds of glycerine with organic acids. They are easily hydrolysed, giving the free acids and glycerine. The conditions which effect this decomposition vary according to the oil in question, in many cases the normal atmospheric influences will suffice to turn an oil rancid or acid in the course of a few days, or even of a few hours. Moisture and warmth are particularly favourable, and oils which are ordinarily stable are often quickly hydrolysed when boiled with water under pressure, as in a boiler, for example.

The free organic acids, produced as described above from animal and vegetable oils, can attack iron in a similar manner to carbonic acid, the action being cyclic and regenerative. Ferrous salts are first produced, and are then decomposed by oxygen, yielding ferric hydroxide and the original quantity of organic acid. A small quantity of such an oil or grease in a boiler may lead to very serious corrosion, and the use of this class of oil is therefore not to be recommended in cases where it may gain access to the boilers, or where the conditions are conducive to hydrolysis, for instance, contact with hot or alkaline waters.

Hydrocarbon or mineral oils, which consist simply of hydrogen and carbon, are unaffected by water, and their use is preferable to that of fatty oils, etc. They can, however, develop acidity, though by a different process from that which results in acidity in fatty oils. Prolonged exposure at an elevated temperature to the air causes the formation of acid products (known in certain cases as sludge) due to oxidation, and which are capable of attacking iron and copper. The degree or amount of acidity produced per unit quantity of oil varies greatly with different grades, but never reaches the same proportions as obtain with fatty oils. Moreover, in practice the mineral oils are generally used up and replaced before they have time to develop any appreciable acidity.

The discriminate use of fatty oils and the examination of lubricating oils for fatty adulteration, in which should also be included rosin and rosin-oil adulteration, should receive careful attention if attempts to minimise the risks of corrosion are to be conscientious.

CHAPTER V

THE INFLUENCE OF THE ELECTROLYTE ON THE CORROSION OF IRON

SINCE the corrosion of iron is due primarily to attack by hydrogen ions, it may be anticipated that acid media will have a pronounced stimulative action on corrosion and, conversely, that alkaline media will inhibit or arrest corrosion. The influence of saline media is not so readily predicted, though they might reasonably be expected to accelerate corrosion, if only because their presence is conducive to ionic activity and may thus facilitate electrolytic action. Salts resulting from the combination of a strong acid with a weak base hydrolyse in solution and produce definite concentrations of hydrogen ions; in other words, they yield an acid solution. Such salts should, of course, be looked upon as acids so far as their influence on corrosion is concerned.

As a general rule each of these anticipations is verified in practice; electrolytes which give acid solutions stimulate corrosion, and those which give alkaline solutions (*i.e.* produce hydroxyl ions) inhibit corrosion, and may, if the concentration of hydroxyl ions be high enough, entirely prevent corrosion. Exceptions to these generalities are numerous, however, and result in anomalies whose consideration is of particular importance, since cases of practical corrosion are frequently influenced thereby in an unexpected manner.

The action of acid solutions on iron is invariably a solvent one. Even the production of the passive state by immersion in strong nitric acid may be regarded as a process which is initially one of solution, for if the passivity so induced is the result of the formation of a tenuous film of metallic oxide, it is conceivable that the iron content of this film must first have gone into solution prior to becoming oxidised and redeposited on the parent metal. The first products of acid attack are a ferrous salt and gaseous hydrogen. In most cases, the latter escapes as gas, but if the acid be also an oxidising agent for instance, nitric acid the hydrogen may be oxidised to form water as quickly as it is evolved. Moreover, in such a case, the final product of the acid attack is a ferric salt, the excess of acid oxidising the primarily produced ferrous salt.

This oxidation, in the case of non-oxidising acids, such as hydrochloric acid, is dependent upon atmospheric oxygen, and the nature of the final product is here determined by the quantity of acid present relative to the amount of metal. If the acid is in excess, the soluble ferric chloride will result, but if, on the other hand, the quantity of acid is small, then the action of oxygen will be to precipitate the ferrous chloride as rust, liberating, of course, the free acid. The two cases may be illustrated as follows :—

$$(28)\quad \left.\begin{array}{l}(a)\ 4Fe + 8HCl = 4FeCl_2 + 4H_2 \\ (b)\ 4FeCl_2 + 4HCl + O_2 = 4FeCl_3 + 2H_2O\end{array}\right\}\text{excess of acid}$$

$$(29)\quad \left.\begin{array}{l}(a)\ 4Fe + 8HCl = 4FeCl_2 + 4H_2 \\ (b)\ 4FeCl_2 + O_2 + 10H_2O = 4Fe(OH)_3 + 8HCl\end{array}\right\}\text{trace of acid}$$

It is possible that the oxidation shown in equation 28 (*b*) may occur even when the amount of acid is small, but the ferric chloride thus produced would, in this case, attack the iron and so become reduced again to ferrous chloride, the reaction being essentially as shown below :—

$$(30)\quad 2FeCl_3 + Fe = 3FeCl_2$$

Sulphuric acid produces in similar manner ferrous sulphate. This salt is not so readily oxidised as the chloride, so that the solution of iron in dilute sulphuric acid is not so rapid as in hydrochloric acid of the same ionic concentration. Ferrous sulphate is insoluble in concentrated sulphuric acid, and under these conditions the metal becomes covered with a protective layer of its salt, which retards its further solution.

The action of phosphoric acid is, to some extent, comparable to that of strong sulphuric acid, the products of its attack are insoluble and, by clinging to the metal surface, afford protection against further attack. The resistivity which a phosphorus content sometimes appears to confer on iron and steel is no doubt due in some measure to this fact. During corrosion the phosphorus may be oxidised to phosphoric acid, which, by its attack on the metal, produces the protective covering described above. Under suitable conditions a phosphatic coating can be produced in such a hard, compact, and adherent form that it provides a permanent protection to the metal against the generally occurring corrosive influences. The commercial process known as " Coslettising " is a technical application of this.

The action of carbonic acid on iron is analogous to that of hydrochloric acid in dilute solution, the ferrous carbonate, or it may be the bicarbonate, first produced, is precipitated as rust by the atmospheric oxygen. The effects of an excess of carbonic acid, in the absence of oxygen, have already been described in Chapter II. Carbonic acid is seldom, if ever, absent in practice, and although it is generally considered to be a weak acid, its effect, even in the absence of other contributory corrosive influences, is very considerable, and where the supply of oxygen is not restricted, corrosion can proceed at a very rapid rate through the action of this acid alone. The reason lies in the fact that the ferrous carbonate is very easily decomposed by oxygen, more readily than any of the other common ferrous salts, and consequently the regeneration of the carbonic acid is quickly ensured and the solution of the iron is able to proceed at a steady rate. In the case of very dilute hydrochloric acid, the latter will continue to dissolve the metal until it is almost expended, and, as its regeneration from the ferrous chloride is so much slower than is the case with ferrous carbonate, a lower concentration of acid is maintained.

Nitric acid, in concentrations other than those which induce passivity, has the usual strong solvent action upon iron, coupled with its oxidising properties. Chromic acid is also an oxidiser, but its behaviour towards corrosion processes offers a striking contrast to that of other acids. It does not stimulate corrosion, but inhibits the process, and the same property is exhibited by its salts, the chromates, and bichromates. This phenomenon is usually explained as the result of the passivifying action of chromic acid and its salts, and if the Oxide theory of Passivity is accepted, the explanation is a reasonable one, especially if it be also assumed that the oxide film is insoluble in chromic acid. It is rather difficult, however, to co-ordinate this interpretation with the fact that the concentrations of chromic acid necessary to prohibit corrosion are extremely low.

The very marked inhibiting action of chromic acid, even in exceedingly dilute solution, will be referred to later in connection with the influence of chromates and bichromates for which Friend has recently offered a fuller explanation in line with his Colloid theory of corrosion.

Iron will not corrode in alkaline media unless the concentration of alkali be very low. The influence of alkalies is inhibitive, and corrosion may be entirely prevented by suitable concentrations. Several explanations have been advanced to account for this, and each of them presents a partial interpretation of the facts. According to the Acid theory of corrosion, the inhibitive action of alkaline hydroxides is due to their absorption and consequent fixation of the atmospheric carbon dioxide. This is, of course, indisputable and is no doubt one of the factors which adds to the nett effect exhibited by the alkali. The Electro-chemical explanation is more comprehensive; it points out that hydrogen ions and hydroxyl ions cannot exist in the same solution at the same time if the latter are in excess, nor can hydrogen ions be formed in such a solution. Corrosion cannot therefore proceed on iron immersed in it. If the concentration of hydroxyl ions is not sufficiently in excess, then potential differences may segregate the hydrogen ions from the hydroxyl ions and corrosion can occur locally. This offers some explanation why very dilute solutions of alkalies do not prevent corrosion and also why the corrosion which occurs under such conditions frequently takes the form of pitting.

Friend considers that the precipitating action of the electro-negative hydroxyl ion on the catalysing and electro-positive ferric hydroxide sol (Chapter II.) offers the most satisfactory explanation. The precipitation of a positive colloid requires a definite minimum concentration of an electro-negative ion. Hence, until the concentration of the alkali is sufficient to give this minimum, no precipitation of the sol occurs and corrosion proceeds. For this reason very dilute alkaline solutions do not prevent corrosion, but have actually a stimulative action. The minimum concentrations, beyond which corrosion is prohibited, are low, being 1·0 gramme per litre in the case of sodium carbonate, and 0·1 to 0·3 per cent. in the case of potassium hydroxide (Friend, *The Corrosion of Iron and Steel*).

Friend has also been able to put forward, on the above lines, a satisfactory explanation of the influence of salts on corrosion, a matter which hitherto had been but incompletely understood. Excluding acidic and basic salts, which should really be included with acids and alkalies respectively, since in solution they hydrolyse and produce acid and alkaline media, the action of salts is chiefly dependent upon *their concentration. If this is sufficiently high, then corrosion may be retarded or even completely arrested, whilst low concentrations* almost invariably cause an increase in the rate of corrosion. If relative corrosion be plotted against the concentration of the salt, a curve is obtained which is usually of the type shown in fig. 8. The point *A* on the ordinate represents the rate of corrosion in pure water.

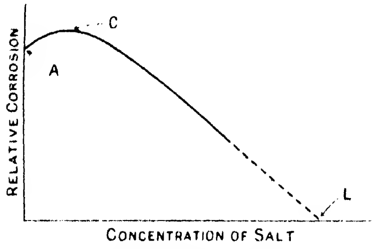

Fig. 8.—Showing the Influence of Saline Concentration on the Rate of Corrosion.

As the concentration of the salt is increased from zero up to the point *C*, the rate of corrosion increases also and reaches a maximum at this point. Further increase in the concentration of the salt then commences to bring about a reduction in the rate of corrosion, and complete prohibition results when the concentration reaches that represented by the point *L*. This value is known as the "Limiting" concentration, and that which coincides with the maximum rate of corrosion is known as the "Critical" concentration. In some cases the point *L* lies beyond the point of saturation of the salt, and it then becomes a hypothetical value and the complete prevention of corrosion is never effected by those salts to which this applies.

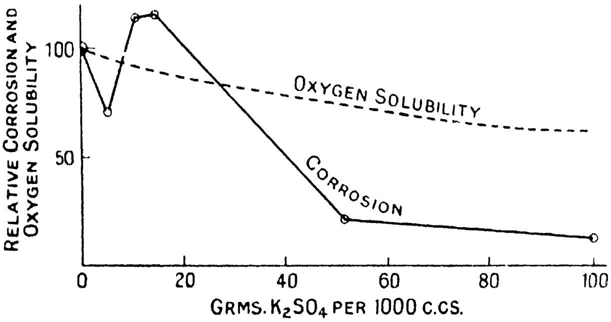

Fig. 9.—Showing the Influence of Saline Concentration on the Solubility of Oxygen and on the Rate of Corrosion.

This behaviour of neutral salts has been recognised for some time, and their inhibiting influence was assumed to be due to the decreasing solubility of oxygen which occurs in saline solutions as the concentration of the salt increases. The preliminary increase in the rate of corrosion was not understood, and no satisfactory explanation was advanced to account for it. It has been shown, however, that the reduction in the rate of corrosion is not proportional to the reduction in the solubility of oxygen in the salt solution, being, in fact, much more rapid. Thus the rate of corrosion may be reduced to a value almost approaching *nil* by a salt concentration which reduces the oxygen solubility by only 40 to 50 per cent. of that in pure water. Fig. 9, which is reproduced from *The Corrosion of Iron and Steel*, by J. N. Friend, illustrates this in the case of potassium sulphate.

The values of the limiting concentrations of salts have been shown to decrease with increase in the valency of their electro-negative ions, so that whereas comparatively high concentrations of monovalent ions are necessary to prevent corrosion, relatively low concentrations of divalent ions suffice.

The explanation advanced by Friend (*The Corrosion of Iron*, Carnegie Scholarship Memoirs, Vol. XI., 1922) to interpret these variations in the behaviour of different salts and of different concentrations of the same salt is as follows: Until the critical concentration is reached corrosion is stimulated in a manner similar to that already described in connection with alkalies. When the concentration corresponding to the point *C* is exceeded, the precipitating action of the electro-negative radicles of the salt comes into play and a retardation of corrosion results which is increased as the concentration of the salt approaches *L*, where absolute prohibition occurs if, as already mentioned, the limiting concentration is below that of saturation. The differences exhibited by various salts whose precipitating ions differ in valency are shown by Friend to be in agreement with the figures given by Linder and Picton, who investigated the relative precipitating powers of various negative ions and found them to have the following ratio:

Chromates and Bichromates .	1000
Sulphates	670
Chlorides and Nitrates . .	3

He points out that, by considering the problem in this way, it is easily understood why very small concentrations of chromates and bichromates have such extraordinary inhibitive powers and why the concentrations of common salt and other chlorides, etc., necessary to produce an appreciable retardation of corrosion are relatively so high. With regard to chromates and bichromates, this explanation seems to be much more satisfactory than the one which attributes "passivifying" properties to such dilute solutions of these salts.

It will be remembered that the effect of increase in temperature on the rate of corrosion in pure water is two-fold. The presence of dissolved salts adds, however, a further complication due to the fact that increase in temperature reduces the value of the critical concentration, and in this direction, therefore, tends to reduce the rate of corrosion.

When two or more salts are present at the same time the problem becomes still further involved. There may be, for instance, one salt whose concentration is below the critical point, and another whose action is inhibitive. Inter-reaction may take place between the salts and result in one case in the production of an acid solution

and in another case in the production of an alkaline solution. For example, when potassium bichromate and common salt are present together, a condition of equilibrium is established in which hydrochloric acid is produced :—

$$(31)\quad K_2Cr_2O_7 + 2NaCl + H_2O \rightleftharpoons K_2CrO_4 + Na_2CrO_4 + 2HCl$$

Two contending factors thus result, the stimulating acid and the inhibiting chromates, and since the removal of the acid by its attack on the iron would cause the reaction to proceed continuously towards the right, it would seem that such a combination of salts would have a nett stimulative effect.

The influence of dissolved salts is perhaps of greatest importance when they occur in boiler-feed waters, etc., for under boiler conditions their action is not only detrimental to the boiler itself, but may extend and be equally detrimental to practically every unit of the plant. They will therefore receive more specialised treatment later in this connection. Their presence is not so vitally important in so far as structural and other material is concerned, since such is more readily protected by paints and metallic coatings than is the case with the metal used in the construction of steam-raising and allied units. Friend, however, deals with the action of single salts and of mixtures of salts in a very complete manner in his book, *The Corrosion of Iron and Steel*, and those who wish to follow this problem further than is possible from the short account which constitutes this chapter are referred to this authority. Also a detailed representation of the Colloid theory of Corrosion as applied to the effects of dissolved salts may be consulted in *The Corrosion of Iron*, Carnegie Scholarship Memoirs, Vol. XI., 1922, by the same author.

CHAPTER VI

THE INFLUENCE ON CORROSION OF FACTORS INHERENT IN THE METAL

It is not proposed to discuss the general relative corrodibilities of the various types of iron and steel. The behaviour of any one type presents a very wide range of variation under different conditions, and, moreover, each type is represented by products which may be classed as "good," "bad" or "indifferent" in quality. A comparison between even the "good" representatives of the numerous types is very difficult to make, chiefly because of the large number of alternatives available upon which to base a comparison. To compare the relative corrodibilities, for instance, in pure water, or other standard electrolyte, and under standardised conditions of temperature and aëration, etc., and to tabulate the results so obtained, would be of little or no practical value, since the application of such a classification would obviously not extend to any set of conditions other than those under which the data for its compilation was determined.

It has been repeatedly observed that conditions which favour an extremely rapid corrosion of one kind of material are particularly well withstood by a second variety of material, and that if these conditions are then altered or modified, the metal which previously suffered the more severely may then prove superior in its resistance to corrosion to the one to which it was originally inferior. It is unprofitable, therefore, to attempt to reach a conclusion as to the general relative corrodibilities of ferrous materials, and it is the present tendency to attach importance more to the relative suitabilities of materials under the particular conditions to which they will be exposed whilst in service. Information of this character is more readily obtained by the consumer and is of direct and immediate value. If the results of reasonably large scale field tests, made under actual service conditions, are consulted, together with the records of practical experience, in the choice of material for a specific purpose, it will generally be found that, when employed in their proper spheres, so to speak, there is little to choose between the varieties of iron or steel as regards their relative corrodibilities.

Friend (*Carnegie Scholarship Memoirs*, Vol. XI., 1922) surveys the work that has been carried out by various investigators on the relative corrodibilities of iron and steel, and those who wish for more detailed information on this phase of the corrosion problem are referred to this work. In the *Transactions of The Faraday Society*, Vol. XI., 1915, the same author again discusses the question of relative corrodibilities in considerable detail, and illustrates very clearly the difficulties besetting any generalisation of the degrees of corrodibility. He concludes in the following manner:—

> "Our task therefore resolves itself into a wider problem, not so much as to whether iron is better than steel or *vice versa*, but, rather, which is the best variety of iron or of steel for any particular purpose."

It will be remembered that in Chapter IV., the third group of factors which influence the rate of corrosion was defined as "Factors Inherent in the Metal Itself." These will now be considered. They may be summarised in the following manner:—

(*a*) The presence of alloyed metals and the generally occurring constituents of a non-metallic character such as carbon and sulphur.
(*b*) The presence of surface impurities or extraneous matter.
(*c*) Heterogeneity of structure or segregation.
(*d*) Physical heterogeneity or localised strains.

The Influence of Metallic and Non-metallic Constituents.—That variations in the composition of the metal have appreciable influence on the rate at which corrosion proceeds has long been recognised, and a considerable amount of careful and systematic research has been conducted with a view to obtaining both qualitative and quantitative information in this direction. Unfortunately, however, there has been little or no co-ordination between the individual workers, with the result that their observations are often difficult to correlate and compare. A common basis of comparison is lacking. With but comparatively few exceptions, the information regarding the effect on corrosion of the presence of other metals and constituents is of a qualitative nature only, and to discuss this question in any other way would not be justifiable nor possible.

It will be convenient to consider first the influences of certain constituents which are always present in iron or steel, irrespective of the particular type of material.

Carbon. The effect of carbon on the rate of corrosion will be determined by its quantity and its condition, particularly the latter. Carbon may be present in iron in several forms. As graphite, which may occur as clearly defined flakes of appreciable size, or in a very finely divided condition. In these cases the carbon is free or uncombined. Combined, or carbide carbon, occurs as pearlite, troostite, martensite, etc., and also in a somewhat obscure form which gives rise to the production of hydrocarbons when the metal containing it is treated with hydrochloric acid.

Each variety has its characteristic influence on the corrodibility of the metal, and a very wide field of inquiry is thus presented and, to repeat a statement which unfortunately occurs so frequently in connection with corrosion problems as to become monotonous, the information available is scanty and, to a large extent, contradictory. It should be remembered, however, that the influence of carbon is considerably modified by the treatment accorded to the metal, *e.g.*, heat-treatment and tempering, etc.

With regard to steel, it would seem that the corrodibility of annealed steel increases with the carbon content up to about 0·89 per cent., and then decreases.

In quenched and tempered steels, however, no variation in the corrodibility has been noticed up to 0·96 per cent. of carbon.

Free carbon in the form of graphitic flakes may readily be conceived to accelerate corrosion by providing points of lower potential than the metal, and thereby stimulating galvanic action. There would appear to be a general acceptance of the fact that "hardening" carbon acts in the reverse direction and retards corrosion (Parker, *J. Iron and Steel Inst.*, 1881, **1**, 39). Also white cast iron which contains its carbon in a finely divided condition, and is close-grained, is much less susceptible to attack in acid media than are those irons in which the carbon occurs in the form of well-developed flakes of graphite.

"Graphitisation" is a form of corrosion peculiar to cast iron, and as a result of which the corroding metal becomes covered with a layer of graphite, which preserves the appearance and shape of the original metal. The mass is soft enough to be cut with a knife, and the metal, being oxidised to ferrous oxide, fills the interspaces of the residual mass of graphite. This type of corrosion does not occur with the purer forms of iron, though certain instances are recorded in which wrought iron has been corroded in this manner by prolonged immersion in sea water. It may be that in these cases the carbon content was much in excess of the normal amount.

Graphitic corrosion frequently occurs on buried cast-iron pipe lines, sometimes generally and sometimes in localised portions of the metal. The graphitisation leaves the shape of the pipe unaltered, whereas in steel and wrought-iron pipes, in which the corrosion usually takes the form of pitting, the corroded material or products are generally carried away. Cast-iron economiser tubes have also been known to suffer from graphitic corrosion.

Silicon. The presence of this element in amounts exceeding about 3·0 per cent. has a marked effect in increasing the resistivity of the iron or steel containing it, and products having high percentages of silicon have been marketed as non-corrodible metals. Experiments made by Jouve (*J. Iron and Steel Inst.*, 1908, **1**, 109) showed that iron containing 20·6 per cent. of silicon lost but 0·06 per cent. in weight when exposed to hot sulphuric acid for two months, whereas a sample of material containing 3·0 per cent. of silicon lost 11·6 per cent. in weight under similar conditions. Cast iron lost 46 per cent. in two hours only. The inhibitive influence of silicon does not seem to become appreciable until the quantity present exceeds 2·5 to 3·0 per cent. and its occurrence in smaller quantities may actually increase the tendency towards corrosion. The normal silicon content of steels is not very high, however, and it probably exerts but little influence so far as corrosion is concerned, but such influence is more likely to be disadvantageous than otherwise. High silicon contents impart increased resistivity mainly against acid attack and not towards atmospheric corrosion, which may be enhanced. The principal constituent of metal containing a large percentage of silicon becomes an iron-silicon compound, and its resistance towards acids is probably attributable to this. Further, the presence of silicon in quantities sufficient to have any reasonable inhibitive influence is accompanied by the serious disadvantage that such amounts render the metal brittle and difficult to work, and so restricts its sphere of useful service.

Sulphur.—There is little room for doubt that sulphur has a stimulating influence on corrosion processes and that this influence is directly proportional to the amount of sulphur present. In good-quality steel, any sulphur is contained as manganese sulphide, and provided that this compound is evenly distributed throughout the mass of the metal, its influence becomes considerably modified. Inferior steels may be deficient in manganese, and in these the excess sulphur is combined with iron as ferrous sulphide. It is difficult completely to avoid the segregation of these sulphides during the manufacture of the steel, and the heterogeneity so produced is an aid to galvanic action, for it is known that manganese sulphide and iron sulphide show a different potential to iron. Further, once corrosion has commenced, the sulphur becomes oxidised to sulphuric acid, which, of course, greatly accelerates the subsequent corrosion. In the formation of rust cones, this acid is frequently trapped inside the cone of ferric hydrate, and it is thus readily understood why pitting proceeds so rapidly in many instances. In fact, the corrosion occurring on materials in which the sulphides are segregated frequently takes the form of pitting, and this will naturally be most pronounced under a stagnant condition of the electrolyte. In such cases, the acid concentration may increase considerably owing to the cyclic or regenerative nature of the process:—

$$(32)\quad \begin{array}{l} (a)\ 2Fe + 2H_2SO_4 = 2FeSO_4 + 2H_2. \\ (b)\ 2FeSO_4 + 5H_2O + O = 2H_2SO_4 + 2Fe(OH)_3 \end{array}$$

Ferrous sulphide is very readily oxidised to ferric hydroxide and sulphuric acid. If a piece be powdered and placed in a beaker and covered with distilled water, the presence of soluble sulphate may be detected in the course of a few hours.

In the case of sulphur, then, the influence on corrosion is two-fold, but most significance attaches to the fact that one of the products of the corrosion is itself a particularly active initiator and accelerator of corrosion.

Phosphorus.—The phosphorus content of steel affects the mechanical properties to so great an extent that the permissible or specified amount is low. Its effect on corrosion would appear to be beneficial rather than otherwise, and the greater percentage of phosphorus present in common iron has been considered to be responsible for the somewhat increased resistivity of this class of material compared with the more refined grades of iron and steel. Like sulphur, phosphorus is oxidised to an acid during corrosion, but in this case the products resulting from the action of the acid on the metal are insoluble, and may, under suitable conditions, adhere to the surface of the latter as a slime which affords some measure of protection against further attack.

Unequal distribution of phosphides in the metal will, of course, accelerate galvanic action, and phosphorus may in this way be responsible for accelerating the rate of corrosion. It is obvious, however, that the segregation of any constituent will confer upon it stimulative properties and thereby mask its individual influence. The case of manganese is particularly illustrative of this.

Manganese.—This element has a bad reputation with regard to its influence on corrosion, but it is now generally conceded that the evils attributed to manganese are due to the element with which it is associated in the steel, and not to the manganese itself, whose influence is negligible. Manganese is added to the melt to remove sulphur, and most of it passes away in the slag as manganese sulphide. It is the portion of this compound remaining in the metal which is responsible for the increased susceptibility to corrosion. During the cooling of the metal the sulphide segregates, producing a heterogeneous structure which, in the presence of an electrolyte, results in the establishing of points of different potential. As corrosion proceeds, the manganese sulphide is oxidised to manganous or manganic hydroxide and sulphuric acid, and hence the remarks made in connection with the influence of sulphur are equally applicable here.

Steels containing very high percentages of manganese are very resistant, but such material, ferro-manganese, falls in the same category as ferro silicon, since these products cannot be considered as steel, but should be regarded as special alloys which are probably stable eutectics. There are several other very highly resistant alloy steels which should be included in this class of material, *e.g.*, those containing excessive amounts of tungsten, nickel, chromium, and vanadium.

The influences of alloyed metals on the corrodibility of the product will now be dealt with alphabetically.

Aluminium. Samples of pure iron containing respectively 0·067 per cent. and 1·33 per cent. of aluminium were prepared by Burgess and Aston (*Trans. Amer. Electro-chem. Soc.*, 1913, 22). The behaviour of the first was found not to differ from that of pure iron when exposed to corrosive conditions. The second sample showed an increased susceptibility to attack in acid media but a slightly increased resistivity towards atmospheric corrosion.

Arsenic. There appears to be no definite or conclusive evidence available, regarding the resistance of arsenical iron or steel to corrosion. Heyn and Bauer (*J. Iron and Steel Inst.*, 1909, **1**, 109) made a series of experiments which seemed to indicate that the presence of arsenic led to more vigorous corrosion, but they draw attention to the inconclusiveness of their results, since the specimens were prepared in such a way that their behaviour could not be regarded as likely to correspond with that of steel in which the arsenic was homogeneously distributed. Their material was given an arseniuretted skin by heating it in an atmosphere of arseniuretted hydrogen. Burgess and Aston (*Trans. Amer. Electrochem. Soc.*, 1913, 22) have more recently investigated this problem, and their observations are more or less in accord with those of Heyn and Bauer. It would seem that the arsenic confers no special resistivity against atmospheric corrosion and that the resistance towards acid media decreases slightly with increase in the arsenic content. In any case, however, arsenic has but little significance in this connection, since metals containing it in amounts exceeding unavoidable traces have poor mechanical properties, being weak and brittle and unsuited for most purposes.

Chromium.—Aitchison (*Trans. Faraday Soc.*, 1915, **11**) records some interesting observations on the influence of this metal, and these would appear to have been substantiated by other workers. Up to a certain point (about 10 per cent. of chromium) the addition of this element induces an increased corrodibility, but when this quantity is exceeded, a decidedly increased resistivity is exhibited. Steels containing 19·5 per cent. of chromium were not attacked at all in salt solutions, and only very slightly in 1·0 per cent. sulphuric acid. Continued increase in the chromium content was accompanied by an increased resistivity of the steel, though a small increase in the corrodibility was again observed in the metals of the highest chromium content. In 10 per cent. sulphuric acid, however, the rate of corrosion or solution was found to increase with increase of chromium over 10 per cent.

Cobalt.—*Steels containing cobalt do not present any striking modification in their corrodibilities as compared with that of cobalt-free steel.* Increase in the cobalt content induces a slight but steadily increasing resistivity towards corrosion both in acid media and under atmospheric influences. The introduction of similar amounts of nickel has a much more pronounced effect, and having regard to the much higher cost of cobalt and the quantity which would be required to impart any reasonable resistivity to the steel, there would not appear to be any advantage attending its use in this direction.

Copper.—The effect of copper on the corrodibility of steel is still a question in connection with which there is much controversy, and in spite of the fact that the results of more recent investigations point to the fact that the addition of copper is beneficial, its presence is often viewed with suspicion. Aitchison (*Trans. Faraday Soc.*, 1915, **11**) observed that although the presence of copper resulted in an increase in the rate of corrosion in sodium chloride solutions (the concentration of chloride approximating to that occurring in sea water), and in 1·0 per cent. sulphuric acid, the corrodibility in stronger acid was distinctly lowered and that the rapidity of attack decreased as the percentage of copper was increased. He attributes the enhanced resistivity to the production of a layer of copper on the metal surface, which may actually be observed and which has been precipitated on to the metal from the acid into which it has first gone into solution. Such a film may easily be conceived to act as a protection against further attack, and the greater the percentage of copper in the metal the more substantial may this film become and the more rapidly may it be deposited.

Burgess and Aston (*Trans. Amer. Electrochem. Soc.*, 1913, **22**) are also in agreement with Aitchison in that they consider the presence of copper to enhance the resistivity towards acid attack and also towards atmospheric corrosion. They conducted experiments with steels whose copper contents ranged from 0·089 to 7·05 per cent., and their observations are quite in line with the above. They found that even small amounts of copper resulted in a decidedly improved behaviour. The explanation advanced by these workers is that since iron and copper, up to about 3·0 per cent. of the latter, form solid solutions, it is to be anticipated that the alloy will be perfectly homogeneous, so that influences tending towards galvanic action should be absent or at least at a minimum. The solid solution of iron and copper may lower the solution pressure of the iron, but if this metal goes into solution it will leave a deposit of copper in the form of a protective film on the surface of the underlying metal.

Hadfield (*Proc. Roy. Soc.*, 1922, **101**, 472) also found that a small percentage of copper in steel is beneficial. An increased resistance to atmospheric corrosion, particularly sulphurous atmospheres, was observed. It was also noted that steel with the mill- or rolling-scale removed was more resistant than steel on which the scale was allowed to remain. Steel containing 0·268 per cent. of copper was found to be more resistant to sea water than ordinary steel, particularly as regards the initial rate of corrosion, and the superiority is preserved during subsequent periods of the process. The initial rate of corrosion in 50 per cent. sulphuric acid was rapid with both ordinary and copper steels, but after three weeks' exposure the latter corroded only very slowly, whilst the rate of corrosion of the ordinary steel remained undiminished. Tests made with 20 per cent. sulphuric acid were in agreement with the above, but it was found that there was little superiority in the copper steel as regards its attack by sea water.

The addition of copper up to 1 or 2 per cent. has advantages also in regard to the mechanical properties of the steel, and the latter is comparable to metal in which the copper has been replaced by an equal amount of nickel both as regards mechanical properties and lowered susceptibility to corrosion. Copper steels therefore merit special attention, particularly since copper is cheap and easily added.

Nickel.—It is generally accepted that the addition of nickel to steel very considerably lowers the corrodibility of the metal. Occasional contradictory statements may be found in the literature available, but these are negatived in every direction by the records of the behaviour of such metal in practice. Its corrosion is more difficultly induced or initiated, and it is generally recorded that the subsequent progress of corrosion is also much retarded. Steel containing about 5 per cent. of nickel has proved itself to be so superior in its resistivity as compared with nickel-free steel that considerable quantities of it are used in cases where high resistivity is desired, and in many instances where ordinary steel has suffered extremely rapid corrosion, the substitution for it of nickel steel has very effectively cut down replacement costs, etc.

The results of independent investigators who have made comparative tests on the resistivity of nickel steel are very consistent, and it cannot be disputed that the presence of nickel, in amounts of 1 per cent. and over, does confer a pronounced resistivity towards corrosive attack, both in acid media and under atmospheric conditions, and also that this resistance increases with increase in the nickel content. A very sensible reduction in the rate of corrosion has been observed in steels containing 3 per cent. of nickel, whilst those containing 10 per cent. and more appear to be almost incorrodible. Commercial nickel steels usually contain about 5 per cent.; quantities in excess of this result in a product which is expensive and which is so hard that it is difficult to work.

The protective influence of nickel may be explained in a manner similar to that of copper, *i.e.*, a solid solution of iron and nickel is present which, in the event of corrosion, results in the solution of the iron and a concentration of the residual nickel as a protective film on the metal surface.

Selenium, Silver, Tin, and Lead.—Very few experiments appear to have been conducted with a view to obtaining data on the influence of these metals, probably because they are unusual constituents of steel and because metals containing them would be either too expensive or deficient in mechanical properties to justify their industrial application. Sufficient evidence is not available, then, to warrant any definite conclusions as regards the influence exerted by these metals, although it is interesting to note, in view of the practice of applying protection to iron by tinning and which possibly may result in the formation of a superficial iron-tin alloy, that Burgess and Aston found that increase in the tin content lowers the resistivity to acid attack.

Tungsten.—Aitchison (*Trans. Faraday Soc.*, 1915, **11**) observed that the general corrodibility of tungsten steels increased with the tungsten content up to 21 per cent. of this metal. Further increase in the tungsten produced a decrease in the corrodibility. Investigations made by Burgess and Aston (*Trans. Amer. Electrochem. Soc.*, 1913, **22**) do not confirm Aitchison's results, since they indicate that increase in tungsten results in an increased resistivity. They worked with material in which the tungsten content varied from 0·4 to 23·86 per cent. Attention is drawn, however, to the fact that no pronounced improvement in the resistivity occurs until the quantity of tungsten has considerably exceeded the practical limit, except in so far as the limited application of high tungsten steel to the manufacture of tools is concerned.

Vanadium. The corrodibility of steels containing vanadium is apparently accentuated by increasing proportions of this metal, though little experimental work has been carried out on this class of steel.

The Influence of Surface Impurities or Extraneous Matter.—Mill-scale is perhaps the most important of this group of stimulative factors. It has already been shown (Chapter IV.) that the presence of rust or hydrated ferric oxide, Fe_2O_3, nH_2O, accelerates the rate of corrosion of the iron or steel on whose surface it is produced. The composition of mill-scale is Fe_3O_4, and it might be expected that, owing to its lower degree of oxidation, and consequent less pronounced electro-negativeness towards iron, it would prove a less powerful stimulator than rust. There is abundant evidence to show that this is not the case and that mill-scale is a particularly powerful accelerator of corrosion. This may be explained from a consideration of the difference in the physical characteristics of the two bodies; rust is usually of an open and porous structure and is comparatively loosely attached to its parent metal. On the other hand, mill-scale is extremely hard and dense, and is strongly adherent to the metal. It is, moreover, an excellent conductor of electricity in comparison with the loose textured rust.

A perfectly continuous coating of mill-scale acts as a particularly good protective coating, but if its continuity is broken, as is almost invariably the case on manufactured material, then it promotes electrolytic action and gives rise to rapid corrosion. Pitting is very frequently attributed to mill-scale, and this form of corrosion, although more or less localised, is far more destructive than uniform corrosion, even though the latter be proceeding at a greater rate. A boiler plate or tube, for instance, may lose several pounds in weight under uniform corrosion and yet be little the worse as regards its mechanical strength or fitness for service, but a few ounces, or grammes even, when removed by the localised form of corrosion, pitting, will very soon lead to complete failure of the boiler by almost or completely perforating the plate or tube. It is chiefly for reasons of this kind that mill-scale has acquired its evil reputation, and the evidence generally tends to show that it is thoroughly warranted. If the scale were not so strongly adherent to the metal, corrosion would conceivably result in the formation of rust below the edges of the mill scale where its continuity is broken, and corrosion would proceed along the metal underneath the scale. As the volume of rust is about ten times that of the metal from which it originates, it would push upwards and detach the scale, so that in a short time the process of corrosion would thus have the opportunity of proceeding more uniformly over the entire metal surface. This action of rust, whereby coatings, protective or otherwise, may be detached or removed, is often exhibited on painted material, where it first becomes apparent as a general blistering of the paint film.

It has been demonstrated experimentally by G. C. Whipple and M. C. Whipple (*Trans. Amer. Electrochem. Soc.*, 1912, **22**) that steel which pits badly when the mill-scale is left adhering to it does not pit when the scale has been removed, and the necessity for its removal is now generally appreciated. Good painters always prefer to commence work on a scale-free surface.

Other impurities, such as cinder and slag inclusions, whose occurrence in commercial products is by no means uncommon, and which, although they may be distributed more or less uniformly throughout the mass of the metal, necessarily appear on and destroy the uniform character of the surface, have a similar influence to mill-scale in stimulating galvanic action. Also, during the process of rolling, particles of scale and other impurities become embedded in the metal surface and the corrosion of such material often occurs in parallel lines as a result.

The effect of occluded gases in iron on its corrosion is a question which is often overlooked, yet they cannot be without influence on the corrodibility of the metal. The gases concerned are hydrogen, oxygen, and carbon dioxide. Occluded hydrogen is electro-negative to iron, and the metal can absorb a comparatively large amount of this gas, particularly if the latter enters into combination with it. The action of strong acids, as in pickling, exposure to super-heated heated steam, and quenching in water, result in the occlusion of hydrogen, and the metal, which is also thereby hardened, is known to be readily corrodible. Electrolytic iron does not always behave in accordance with the general supposition that, "the purer the metal, the greater its resistivity," and it is possible that its occluded hydrogen may be responsible for such misbehaviour, or at least that portion of the gas which is present in the free state and not combined with the metal as an iron-hydrogen alloy.

The probable influence of occluded oxygen and carbon dioxide may readily be imagined and need not, therefore, be considered further.

Structural Heterogeneity—Strain.—The influence of segregation has already been introduced in connection with the consideration of the manganese and sulphur contents of steel. The process of corrosion is initially one of solution, and is dependent upon electrolytic conditions which are established on the surface of the metal. If the latter is perfectly homogeneous and free from impurities, there can be no segregation, and the formation of electrolytic couples on its surface cannot result from such a cause. Iron must first go into solution before it can be converted into rust, and in so doing a current must necessarily flow from the point at which iron is dissolving to some other point on the metal surface. Any influence which facilitates the flow of this current will accelerate corrosion, and segregation, therefore, by providing points of lower potential to the iron, tends to induce an increased rate of solution or corrosion by stimulating galvanic activity.

The segregation may be that of impurities or of some essential constituent of the metal, and it follows from the above that the rate of corrosion of the metal will generally increase with increase in the degree of segregation. It should be the aim of steel manufacturers, therefore, to eliminate, as far as possible, all impurities and to exercise careful control of their processes in order that the segregation of essential or unavoidable constituents of the product may be reduced to a minimum. The fact has been repeatedly emphasised and confirmed by actual experiment that, other conditions being equal, the higher the purity and homogeneity of the metal, whether iron or steel, or, in fact, any metal or alloy, the greater is the resistance offered by it towards attack by corrosive influences. The production of such material, however, is by no means easy, and it must be remembered that manufacturers have other objects in view, such for instance, as the good mechanical properties of their products, and concentrated efforts on their part to attain chemical purity and homogeneity, would, in all probability, result in an undesirable modification of these mechanical properties.

In connection with the heterogeneity of the metal, one or two words may be included with regard to heterogeneity of the electrolyte in which it corrodes. It may happen, under certain conditions, that solutions of the same composition but of different concentrations come into contact with adjacent portions of the metal, and what is usually known as a " concentration cell " is produced. That portion of the metal in contact with the more dilute solution of the salt, etc., corrodes, at any rate initially, preferentially to that in contact with the stronger solution. A simple way of illustrating this is to half fill a glass jar with a saturated solution of salt and then to carefully fill up the vessel with a much weaker solution of salt. The difference in the densities of the two solutions will serve to keep them separate for a sufficient length of time in which to perform the experiment. If a strip of iron is then lowered into the jar so that its lower half is wetted by the saturated salt solution and its upper half by the weak salt solution, it will be observed that the corrosion is unmistakably confined to the upper half of the strip.

It is also interesting to note, in connection with the effect of homogeneity and purity, that a highly polished iron or steel surface, especially the latter, offers remarkable resistance to corrosion as compared with an ordinary smooth surface, and particularly with a rough or cast surface. Highly polished steel is very resistant to acids and etches with difficulty, a drop of water placed on it assumes a spheroidal form, and there is, in consequence, a minimum surface of contact between the metal and the electrolyte. It is supposed that the effect of polishing is to spread a film of pure iron over the surface, covering the impurities and segregations, and thereby imparting an enhanced resistivity to the metal. Whether this explanation is correct or not does not alter the above facts, and it has been suggested that it would be worth while to polish the surfaces of boiler and condenser tubes in order to ensure a greater length of service and freedom from corrosion. An alternative explanation of the effect of polishing is that it removes the greater proportion of surface impurities and consolidates the surface rendering it less porous. The lowered rate of corrosion, however, applies almost wholly to the rate of initiation, once it has established a hold on the metal surface, the effect of polishing ceases to operate.

Physical Heterogeneity—Localised Strains.—The fact that a strained portion of a piece of metal exhibits a different potential to the remainder is excellently illustrated by means of the ferroxyl reagent. Figs. 10, 11, and 12 are photographs of pieces of pure iron wire mounted in the reagent. In each case the pieces were cut from the bobbin with scissors, and it will be seen that in fig. 10 the ends of the wires, which have been subjected to a shearing force, have, without exception, developed a zone of blue colour about themselves, showing that the strained metal has acquired a different potential from the rest of the wire, and, in this particular case, a higher potential. Fig. 11 shows a number of pieces of wire, which were also cut from the roll with scissors, but in addition they were each given a sharp blow midway along their length, flattening their sections. Blue zones developed at these points, again showing that the strained metal has a higher

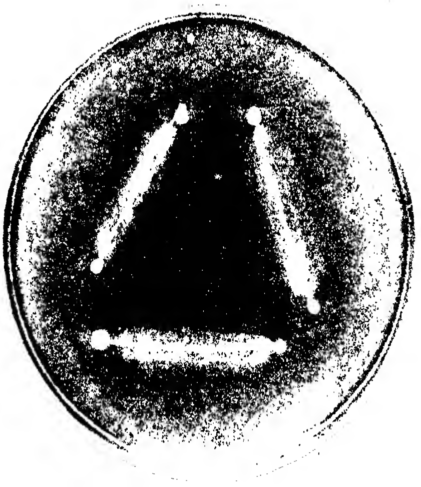

FIG. 10.—STRESSED IRON WIRE MOUNTED IN FERROXYL.

solution pressure than the unstrained metal. It is also interesting to note that, in two of the pieces, the flattened portions are electro-positive to the sheared ends of the wires. In fig. 12, the wires had been repeatedly bent backwards and forwards about their middles before being mounted in the reagent, this treatment corresponding to cold-working, and here, again, a similar difference in potential is exhibited.

Localised internal strains may be produced in the metal in several ways, during the processes of manufacture, the working, and under conditions of service. Modern high-speed methods of production and working, tend to result in products in which segregation is pronounced and which have been cut, pressed, rolled, or machined into shape so rapidly that molecular readjustments have been prevented and internal strains have thereby been developed. Carefully controlled annealing would go far towards eliminating these strains by permitting readjustments in the metal structure, and might be advantageously resorted to wherever possible. The slow cooling and working of metals of olden days has been advanced as one reason why these products are permanent in character as compared with modern products. They were handled slowly and tediously and subjected to prolonged heating and slow working which ensured a greater freedom from strain and heterogeneity by thorough annealing.

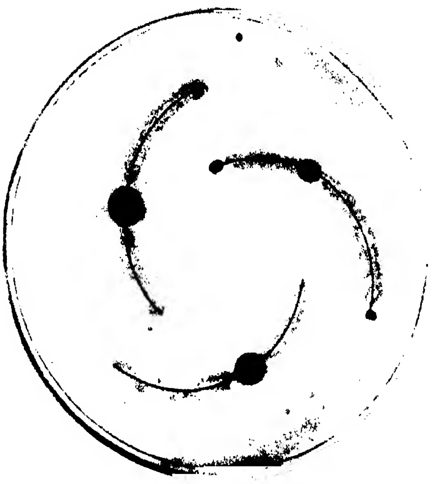

FIG. 11.—STRESSED IRON WIRE MOUNTED IN FERROXYL.

Modern methods of cold-working, with perhaps an occasional exception in the case of porous material which has been cold-rolled, and in which a consolidation of the surface has thus been effected, greatly accelerate the corrodibility of the metal. The immediate vicinity of a punched hole in a steel plate, for instance, is usually the point at which corrosion commences. The grooving of bends and angle irons and the pitting of rivet heads, which commonly occurs in boilers, are again due to the same cause, for although the material may have been heated prior to bending and the rivets to riveting, it has been rapidly cooled and has not been subsequently annealed. A subsidiary cause of grooving in boiler parts is attributable to strains produced thermally, a temperature gradient along a piece of metal will obviously produce internal strain by causing unequal expanison or contraction in adjacent portions.

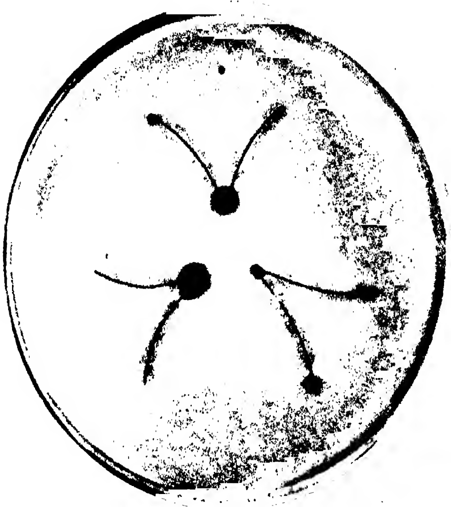

Fig. 12.—Stressed Iron Wire Mounted in Ferroxyl.

Cold-working a metal or working it at temperatures below which recrystallisation cannot proceed results in the production of a film of amorphous material between the crystal grains, and this material is electro-positive to the crystallised portion. The first stages of the corrosion of such material is therefore more pronounced along certain more or less well-defined lines, and the metal, in addition to being strained, has also been given a heterogeneous structure.

It is well known that surface wounds on a metal, such as indentations, scratches, abrasions, etc., and also fractured surfaces, become centres of corrosion. This is readily understood in the light of the foregoing remarks, since the metal must have been locally strained when the wounds were inflicted. Such defects generally exhibit an electro-positive character to the adjacent metal, and it would appear to be the rule that strained portions of a metal always assume this character though the factors determining the relative potentials are in such delicate equilibrium that reversals of polarity are readily and frequently induced.

In concluding this chapter, it may be desirable to summarise the inhibitive and stimulative factors which have so far been discussed.

STIMULATIVE FACTORS

(*a*) Those tending to maintain a high concentration of oxygen at the seat of corrosion.

(*b*) The presence of rust and mill-scale.

(*c*) The presence of electrolytes in the wetting medium.

(*d*) Stray currents from external sources.

(*e*) Contact (as in structures, etc.) with dissimilar metals.

(*f*) Segregation of constituents and the presence of surface impurities.

(*g*) Physical heterogeneity or a condition of internal strain.

(*h*) Surface wounds.

(*i*) Cold-working and other processes or conditions inducing (*g*).

(*j*) The presence of occluded gases.

INHIBITIVE FACTORS

(*a*) Factors tending to limit or cut off the supply of oxygen from the seat of corrosion.

(*b*) The presence of certain electrolytes in sufficient concentration, chromic acid, chromates, and alkalies.

(*c*) The presence of mill-scale in a continuous and unbroken film.

(*d*) Contact with metals having a higher solution pressure.

(*e*) Correctly applied external currents.

(*f*) Control of impurities and care in manufacture with a view to limiting segregation. Annealing.

(*g*) In general, the converse of the factors given in the previous list.

NOTE ON THE CORROSION OF "BUSY" IRON

It has often been noted that iron which is in constant service suffers, in many instances, much less severely from corrosion than does similar material which is "idle." The typical and most frequently quoted example is that of railway lines; those on the main line are always less corroded than those in the sidings or the renewals which may be seen lying alongside the track. The comparative freedom from corrosion is not confined to the top or running surface of the rail, but is shared to a greater or less degree by all portions of the rail surface. Somewhat analogous observations have also been recorded in connection with many cases in which the material is not static, either actually or relatively.

Several explanations have been advanced to explain these facts, and it is probable that each offers a correct, if only a partial, solution. It has been suggested, for instance, that the conditions most favourable to the electrolytic action by which corrosion proceeds are those of an undisturbed or quiescent nature. In some cases of pipe-line corrosion it has been observed that the process is most rapid during the intervals in which the flow is slowest. According to the above suggestion, a slow flow permits the bubbles of dissolved gas, liberated by the water, to cling to the metal surface, whereas a rapid flow would tend to sweep them along with it. In steel pipes, therefore, a slow flow would be conducive to pitting, but a rapid flow would minimise the likelihood of this. This explanation is a reasonable one and, if taken in conjunction with that offered by a consideration of Friend's Colloid theory of corrosion, may well represent the greater portion of the truth, so far as pipe lines are concerned.

The behaviour of "busy" steel rails is, however, most probably attributable to a series of influences. On a busy route, for example, it is quite possible that the frequent passage of traffic maintains the rails at a temperature sensibly above that of the atmosphere, and the moisture contained in the latter would be thus prevented from condensing on them. Further, any rust that may be produced is liable to become detached by the vibration, and the chances of an acceleration of corrosion due to the presence of rust are reduced almost to *nil*. The top surface of the rails are always more or less polished, and even if local electrolytic couples exist on them, it may be that these are frequently disturbed and the polarities reversed by the passage of traffic over them. These probabilities cannot, of course, be extended to other portions of the rails which nevertheless share the immunity from corrosion. The most recent addition to the above suggestions, and which is applicable to all portions of the rail surfaces, comes from Friend, who draws attention to the effect of vibration in precipitating colloids. The vibration of the traffic, according to Friend, precipitates the catalysing ferric hydroxide colloid and in this way retards corrosion.

CHAPTER VII

WATER: ITS SOURCES, CHARACTERISTICS, AND IMPURITIES

Since chemically pure water never occurs naturally, the interest attached to waters centres solely about the impurities they contain and which have been acquired from the materials with which the water has come into contact during its journey from its source (rain, snow, etc.) to the consumer.

Water is essential and indispensable, not only to all forms of life, but to all branches of industry, and its varying characteristics are derived from the impurities, both solid, liquid, and gaseous, which it may contain. It is responsible for many natural phenomena, including, as we have seen, that of corrosion, and under present-day conditions, the suitability of different waters for steam-raising purposes and the methods of improving the qualities of waters for this purpose are problems of very great importance. The durability and economical operation of boilers and of other units of power plants are principally dependent upon the use of a pure boiler-feed water.

Very few natural waters are directly suitable for use as boiler-feed, the majority of them require, and should receive, treatment of some kind if the boilers, etc., are to be maintained in a reasonably clean and corrosion-free condition. Unsuitable water, if used raw, *i.e.*, untreated, may result in serious damage in many ways, amongst which may be mentioned the rapid corrosion of boiler plates, tubes, and fittings, rivet-shearing and the development of leaks through the unequal expansion and contraction which may arise from the excessive overheating caused by heat-insulating deposits, and bulging or "hogging" of tubes, etc. Moreover, the evil effects of using unsuitable water are rarely confined to the boilers alone, but are also manifested in other units of the steam-raising and power plant, from economisers and feed-heaters to the turbines.

Although, strictly speaking, the author intends to deal only with the corrosive constituents of waters, regard will be had for the scale-forming and other deleterious impurities, first for the sake of completeness, and secondly because it is very difficult to draw a sharp line of demarcation between the two classes of impurities. In addition, many methods of water treatment which have been evolved from processes which were originally directed towards the prevention of boiler-scale also eliminate constituents which are now recognised as being corrosive.

The corrosive constituents of waters are principally the salts, other than the carbonate, of lime and magnesia, mineral acids and organic acids, grease and the dissolved atmospheric gases oxygen and carbon dioxide. The chief scale-forming impurities are the carbonates of lime and magnesia, sulphate of lime, and silica. Other salts of a permanently soluble nature may also assist in the formation of scale by their inter-reaction, and the precipitation of the scale-forming carbonates, or rather, bicarbonates, liberates, at the same time, the corrosive carbon dioxide.

Water commences to collect its impurities from the moment it coalesces into drops and falls as rain. In falling to the earth it dissolves quantities of atmospheric gases, principally oxygen and carbon dioxide and nitrogen, but traces of ammonia, nitrous acid, nitric acid, etc., are also almost invariably present. In the vicinity of towns, sulphurous and sulphuric acids and sulphuretted hydrogen are also included and a surprising amount of dissolved and suspended solid matter is in many cases acquired from the dust and soot suspended in the atmosphere. The quantities of dissolved gas contained in rain water varies considerably, but the figures are usually in the neighbourhood of 10 to 15 cubic centimetres of carbon dioxide and 20 to 30 cubic centimetres of oxygen per gallon. The carbon dioxide content, though apparently small, plays an important part in ensuring the further contamination of the water, for, on reaching the ground, the slight acidity conferred on the water by this gas is largely responsible for the disintegration of rocks and silicates and almost wholly for effecting the solution of lime and magnesia as their bicarbonates when the water passes through such geological strata as chalk beds, lime-stones, etc. The silica from the erosion of rocks is taken into solution as such or as the more freely soluble sodium silicate.

The disintegration of rocks is assisted by fluctuations of temperature, particularly over a range which centres about the freezing point, and by the erosive action of running water. Also a preliminary hydrolysis of certain constituents by the water results in local expansion and subsequent disruption. Other impurities, such as sodium chloride, result from direct solution, and the final characteristics of the water are the nett result of its contact with the materials over or through which it has flowed. It is usual, therefore, to classify waters according to the sources from which they are drawn; thus we may have:

(1) Rain water.
(2) River water, fresh or estuarine (tidal).
(3) Spring water.
(4) Well water, deep, artesian or shallow.
(5) Lake water.
(6) Surface water.
(7) Canal water.
(8) Colliery water.
(9) Sea water.

Whilst this method of classification may be particularly useful from certain points of view, it is not very well adapted for comparing the characteristics of waters from a steam-raising standpoint. Commencing with rain water, it is more convenient to discuss generally the impurities likely to occur in waters and how these are acquired. For instance, river, spring, deep-well, lake and colliery waters are all influenced alike by the strata traversed by them, and the method of accumulation, whether in wells or springs, etc., is of secondary significance.

Rain water (*Snow, Hail, Dew, Sleet*).—This is, of course, the purest form of natural water. It has been in contact with the atmosphere only and therefore contains the minimum quantity of dissolved solid matter, hence its popular designation as "soft" water. Rain waters are usually very corrosive, however, owing to the relatively large amounts of dissolved oxygen and carbon dioxide which they contain, frequently they may be almost saturated with respect to the former gas. Subsequent contact with mineral and other matter in the earth may eliminate or "fix" these gases, so that waters which have flowed over or through the ground are generally less contaminated with them than is rain water, and may often be less corrosive in direct consequence. The oxygen is expended in oxidising organic matter of both vegetable and animal origin, and the carbon dioxide in rendering the carbonates of lime and magnesia soluble.

In towns and industrial areas the amount of dissolved impurities contained in rain water is often much higher than would be anticipated; sulphurous and sulphuric acids originating from the combustion of coal, etc., are always present. The amount of sulphuric acid may reach a figure as high as 10 parts per 100,000, or 0·01 per cent. The consequences of such a concentration of acid in water which comes into contact with ferrous material may readily be imagined and the rapid deterioration of building material, such as marbles, sandstones and limestones, has often been attributed to the acidity of rain water. Ammonia and its salts, nitrates, and sulphuretted hydrogen are also usual constituents of rain water in these localities, and the quantities of suspended matter, carbon (soot), and road dust (calcium sulphate, calcium carbonate, magnesium salts, and sodium chloride) are, in many cases, astounding. Common salt is an almost invariable constituent, particularly near the coast, where contamination with sea spray is readily effected. The evaporation of the spray leaves the solid matter contained in it in a very finely divided form, and with favourable winds this may be carried many miles inland, to be finally brought down dissolved in falling rain.

When rain water reaches the earth it either penetrates into the ground or flows over the surface, according to the nature of the ground. In the latter case, the result is usually a so-called "soft" water which contains much suspended matter. The weathering or disintegration of rocky ground, which quickly sheds any rain falling upon it, results in the production of a mud consisting of finely divided or even colloidal siliceous particles, and these, together with other insoluble mineral matter, as well as organic products, are carried along in suspension in the water.

This type of water is frequently represented by shallow-well water, and is simply surface drainage. It is particularly susceptible to contamination with organic matter, both dissolved and suspended, and especially when collected in towns or from cultivated land where sewage and other nitrogenous organic matter can gain access to it. Shallow-well waters are, in consequence, usually characterised by the presence of ammonia, nitrites, and nitrates, the latter representing the final stage of oxidation undergone by the organic matter. Phosphates are also frequently present. The nitrates and nitrites are produced initially as the mineral acids, but in the presence of lime, soda, and magnesia, which are rarely, if ever, absent, they appear as the salts of these metals. The soot carried down by rain often contains ammonium sulphate, and this is converted by carbonate of lime into ammonium carbonate, which can be oxidised to nitric acid. This indicates a second way in which the nitrates of lime and magnesia may be introduced into natural waters, and apart from the industrial pollution of rivers and canals, etc., these processes represent, with but an occasional exception, the only sources of these salts. Their presence in boiler feed-water is very undesirable, and the pollution with the type of organic matter which their presence infers also condemns surface and shallow well-waters so far as human consumption is concerned.

Upland surface waters approximate most closely to rain water. They have experienced the minimum contact with the earth, and are therefore likely to be almost free from dissolved mineral impurity. Any organic matter contained in them will be that resulting from decayed vegetable matter, and hence ammonia and nitrates are rarely found in them. The composition of shallow well waters and the like varies, as may be imagined, between very wide limits, and their successful treatment, prior to their use as boiler-feed, is attended by considerable difficulty.

Much of the surface drainage finds its way directly into rivers and streams. River waters are generally much softer than spring or deep well water, partly from the above cause and partly since, as will be shown, they tend to purify themselves. The longer their course before the point is reached at which tidal influences commence to affect the composition, the purer the water will become, assuming, of course, that industrial pollution does not occur. The quantity of suspended matter, for instance, is dependent upon the rate of flow of the river, and if this is slow, as in summer, or towards the mouth of the river, the amount of suspended matter will be low, though such conditions, on the other hand, obviously tend towards a maximum content of dissolved impurity. The self-purification of river water is effected, therefore, first by the settlement or sedimentation of suspended matter, secondly by aëration, which facilitates the liberation of carbon dioxide and results in the precipitation of the insoluble alkaline-earth carbonates, thirdly by evaporation whereby ammonia is lost, fourthly by aëration again, which removes any sulphuretted hydrogen or other sulphides and precipitates any ferrous salts, and fifthly through bacteriological processes which destroy organic impurities. To these purifying influences may be added the somewhat difficultly estimable effect of light (ultra-violet) and electricity, and finally the paradoxical effects of certain industrial effluents which may neutralise acidity or alkalinity or cause the precipitation of certain dissolved impurities.

From the point at which rivers commence to be affected by the tides, an increasing contamination with sea water occurs. The extent of contamination at a particular point of the river's course is variable, and the variation is largely determined by seasonable influences. The result of a drought is to permit tidal effects to a point which is much higher up the river than normal, a wet season has the reverse effect. The periodical development of boiler and other troubles may often be traced to causes of this kind where the station is running on river water and the variations in composition to which river waters are so liable, introduces many difficulties both in connection with their use and their pre-treatment. The more important constituents of sea water are sodium chloride, magnesium chloride, magnesium sulphate, calcium sulphate, calcium carbonate, and potassium chloride, and none of these are in any way desirable in boiler-feed waters.

In contrast to surface and shallow-well waters there are the spring and deep-well waters, including also artesian-well waters. In the first place, owing to the filtration effected by the various strata through which they have percolated, they are comparatively free from suspended matter. This is a point of no inconsiderable importance. Owing to the absence of alternatives it may be sometimes necessary to use waters containing large quantities of suspended matter for boiler-feed purposes, and finely divided or colloidal matter can cause serious troubles in the boilers and in other units, and its removal is difficult. Processes of filtration are often ineffective, and settlement or sedimentation may be impracticable owing to the length of time required and the prohibitive size of the settling tanks which would be necessary. The use of coagulating agents has almost invariably to be resorted to, and unless these are applied in a proper and systematic manner, they may result in troubles as bad, if not worse, than those arising from the suspended matter itself.

Deep-well waters are also more constant in composition than surface and shallow-well waters. In passing through chalk and limestone beds the water acquires quantities of calcium carbonate, which, though almost insoluble in water alone, is dissolved in the form of the soluble bicarbonate owing to the action of the atmospheric carbon dioxide contained in the water. At the same time, carbonate of magnesia is taken up in a similar manner and in amounts relative to the calcium carbonate, varying, of course, with the proportion of magnesia contained in the chalk. Sulphate of calcium or gypsum is usually taken up from the same strata, and in certain cases the chloride and sulphate of magnesia—for example, when the geological formation marks the site of a dried-up sea-bed.

Relative to shallow-well and surface waters, therefore, deep-well and spring waters, whilst free from suspended matter, and also, it may be noted, from organic matter, contain much dissolved matter, and if they have filtered through a chalk formation, they are usually "hard" waters.

The terms "hard" and "soft" water most probably originated from domestic circles, but they are still retained to differentiate between certain characteristics which have an important bearing on the relative industrial suitabilities of different waters. Hard waters increase the labours of the laundry, etc., whilst soft waters lighten them. Hardness is due to the presence of lime and magnesia, either as carbonate, sulphate, nitrate, or chloride, and in certain cases to the salts of iron, aluminium, and manganese. It is really a measure of the soap-destroying properties of the water. Soap is composed of the soluble sodium or potassium salts of fatty acids. In the presence of lime or magnesium salts an interchange of bases occurs whereby the insoluble salts of lime or magnesium and the fatty acids are produced, and which form a curdy precipitate with no lathering or detergent qualities. Until sufficient soap has been added to a hard water to precipitate all the alkaline-earth metals or other hardening impurities, as organic salts, a lather cannot be produced. Free carbonic acid (*i.e.*, dissolved and uncombined carbonic acid gas) also confers hardness by combining with a portion of the alkali in the soap and liberating an equivalent amount of free acid, thereby destroying the soap.

It is usual to differentiate between what is called the "temporary" hardness and the "permanent" hardness of water. The bicarbonates of lime and magnesia are decomposed by boiling the water and are precipitated as the normal carbonates which are insoluble. The carbon dioxide resulting from this decomposition, together with any free dissolved carbon dioxide, is at the same time expelled, and any iron salts are also precipitated. The reduction in the hardness figure (estimated by means of a standard soap solution under standard conditions) brought about by boiling gives the value of the temporary hardness, whilst any residual hardness is known as the permanent hardness. This latter is due to the presence of salts which are not thrown out of solution by boiling, such as the sulphates, chlorides, and nitrates of lime and magnesia, and the salts of iron and aluminium, which may not be completely precipitated. It is these salts, with the exception of calcium sulphate, which cause corrosion in boilers, and the significance of the permanent hardness figure is, therefore, considerable, and is generally regarded as of much more importance than the temporary hardness figure. Temporary hardness is a measure of the alkaline-earth carbonate content of water, and since the lime salt usually predominates, and is considered to be a scale-forming impurity, hardness figures are generally regarded with considerable respect by those in charge of boilers. The temporary hardness figure indicates, at any rate approximately, the quantity of dissolved impurity which will be precipitated in the boiler, and thus enables some idea to be formed of the amount of scale or sludge which will result from the use of the water in question. An exceptionally high degree of hardness, which does not line up with the amounts of lime and magnesia present, usually indicates the presence of decayed organic matter, resulting in the formation of nitric acid and (or) carbonic acid.

In certain localities there occur strata of a sandy character which consist of hydrated aluminium silicates containing also alkaline or alkaline-earth metals. They are characterised by holding the alkali in a loose and readily soluble form, and have a very important influence on the water which passes through them. The typical and more important or active varieties are known as "zeolites," three of which are given below :—

$Na_2O,Al_2O_3,4SiO_2,2H_2O$, analcite
$Na_2O,Al_2O_3,3SiO_2,2H_2O$, natrolite
$CaO,Al_2O_3,6SiO_2,6H_2O$, stilbite

When water containing lime and magnesium salts percolates through a sodium zeolite stratum there occurs an interchange of basic radicles. The sodium of the zeolite replaces the lime or magnesium in the water, so that on leaving the stratum it contains, instead of lime or magnesium carbonate or sulphate, sodium carbonate or sulphate. The composition of the zeolite itself is altered as shown in equation (33):

$$(33)\ CaCO_3 + Na_2O,Al_2O_3,3SiO_2,2H_2O = Na_2CO_3 + CaO,Al_2O_3,3SiO_2,2H_2O$$

In other cases, percolation through a lime zeolite may result in the water containing calcium chloride in place of sodium chloride.

Zeolites have been produced artificially, and have been applied to the treatment of water for boiler-feed purposes. These will be referred to later.

Where these zeolites strata occur, it is often found that deep-well waters, even though sunk through chalk or limestone formations, are alkaline and soft, due to the presence of sodium salts, which have been introduced by contact with zeolites or similar material and not by contact with strata containing sodium carbonate or other sodium salts.

Waters in which the alkalinity is due to sodium carbonate exert an appreciable solvent action on silica, so that, although the normal solubility of silica is but about one-fifth of a grain per gallon, it may be present to the extent of several grains per gallon in alkaline waters as sodium silicate.

Mineral acidity in waters, unless originating from industrial pollution, is usually caused through the oxidation of pyrites, etc., through which the water has passed. Colliery waters or drainage often have an acid reaction, which is attributable to this, since iron pyrites or sulphide is generally associated with coal seams.

Other mineral impurities, such as barium and potassium salts, are sometimes met with, and are derived from strata containing these elements in various forms of combination. Ammonium salts when present in quantities much in excess of those usually occurring in rain and surface-drainage waters indicates artificial contamination, as also does the presence of such metals as lead, copper, and zinc.

In addition to the organic impurities already mentioned, there are those which occur in and characterise water which has flowed over peat. Peat consists principally of cellulose, $(C_6H_{10}O_5)n$, and the products of its decomposition. Cellulose is particularly stable towards dilute acids and alkalies, but it would appear that biochemical processes can effect the production of various compounds, some of which have an acid reaction, and thus it is that waters from peaty districts are often decidedly acid in character and give positive results when subjected to tests which indicate that the acidity is organic. Whilst a definite conclusion as to the nature of these acids may not be wholly justified, it can be reasonably assumed that humic acids, formic, acetic, and glycollic acids, and possibly oxalic acid, exist, each marking a definite stage in the disintegration of the cellulose, of which the ultimate products are carbonic acid and water.

In the presence of these acids other portions of the peat may be converted into such compounds as cellulose acetate and formate, and any mineral salts present in the water may be transformed into the corresponding organic salts, for instance, calcium formate or acetate. Under boiler conditions, these compounds will be hydrolysed and the liberated free acids, which are volatile, can pass over with the steam. The corrosive influences of such waters are usually enhanced because of their comparative freedom from scale-forming impurities which, first by tending to neutralise acidity, and secondly by producing a scale which may act to some degree as a protection to the boiler plates and tubes against corrosion, would have the effect of suppressing the corrosive nature of the water.

Peaty waters are also often characterised by the presence of organic compounds of iron and of ferrous bicarbonate and phosphate. In comparison with the amounts of dissolved mineral matter present, however, the quantity of organic matter is generally small. Ready oxidation of this kind of impurity is effected in the aërated and porous surface layers of the ground.

CHAPTER VIII

THE BEHAVIOUR OF IMPURITIES IN WATERS USED FOR STEAM-RAISING

THE use of hard or unsuitable boiler-feed water may result in five different types of boiler trouble :—

(1) The formation of scales and incrustations.
(2) The precipitation of sludgy deposits.
(3) The corrosion of boiler plates, tubes and fittings.
(4) Excessive priming and allied troubles.
(5) Actual mechanical failure of tubes and plates.

To these must be added the reduced boiler efficiency as considered from the point of view of fuel consumption. The following figures are estimates of the percentage losses in heat transmission through various thicknesses of scale :—

Thickness of scale.	Per cent. heat loss.
$\frac{1}{50}$th inch.	3 to 5·5
$\frac{1}{20}$th inch.	11·0
$\frac{1}{10}$th inch.	15
$\frac{1}{4}$ inch.	20
$\frac{1}{2}$ inch.	100 to 150

It has been shown that a boiler plate covered with half an inch of scale has to be heated to 750° F. in order to maintain a water temperature of 350° F., that is, to a temperature of 400° F. in excess of that which would obtain on a clean boiler plate. Further, to this wastage of fuel must be added the expense incurred in the cleaning and repairing of the boilers and the losses due to the frequent and excessive blowing down which impure waters may occasion. The cleaning of multi-tube boilers is a difficult and expensive matter, and if the use of unsuitable water is continued, the cleaning is merely a palliative. It may or may not prolong the life of the boiler, but it certainly does not contribute very far towards an increased boiler efficiency.

The impurities commonly occurring in raw boiler-feed water obtained from natural sources, may be roughly divided into four groups :—

(1) Scale-forming impurities.
(2) Sludge-forming impurities.
(3) Corrosive impurities.
(4) Scum-forming impurities (*i.e.*, those which cause priming).

The scale-forming impurities consist principally of the carbonate and sulphate of lime and the carbonate of magnesia. Sludge-forming impurities are usually the suspended matters in the water, both inorganic or mineral, and organic, and also certain dissolved mineral constituents. Magnesium salts, mineral and organic acids (either originally present or produced in the boiler), grease and the dissolved atmospheric gases compose the corrosive constituents, and the scum-forming materials may also be of organic or mineral character, such as high concentrations of soluble soda salts.

In considering the behaviour of the feed-water impurities, the modern high-pressure boiler should be looked upon as a huge autoclave in which the combined effects of temperature and pressure result in the decomposition of and the production of compounds, either directly or by inter-reaction between the impurities, which would not occur under normal conditions or even in the older types of low-pressure boilers. The processes which go on in a boiler cannot be observed, and their course has, in many cases, to be inferred, therefore, from the results which are apparent, for instance, when the boiler is opened up for examination, cleaning or repairs.

Under boiler conditions, normally stable salts may be dissociated or become involved in complex series of reactions, or their solubilities may be so modified that a highly soluble salt is found as a scale on opening up the boiler. Scales may sometimes be found to contain a salt which is not present in the feed-water and which must have been produced by inter-reaction in the boiler. Although the behaviour of the constituents of raw boiler-feed waters is often a matter of conjecture and conclusive experimental evidence is lacking, yet inference and circumstantial evidence are usually sufficiently sound and strong that little room is left for doubt in the generally accepted explanations.

A thoroughly systematic treatment of the behaviours of the individual feed-water impurities and the consequent troubles which are occasioned in the various units of the steam-raising plant is not easy. Troubles manifested in one portion of the plant are often originated in another portion, and the harmful influence of a particular impurity may not be confined to one unit only. It is proposed, therefore, to examine the troubles which are experienced in the different units of the steam-raising plant, commencing with the economisers and taking in turn the boilers, super-heaters, and turbines.

ECONOMISERS

Both scale formation and corrosion can occur in economiser units. The corrosion is due principally to the dissolved gases, oxygen and carbon dioxide, in the make-up, or to any acidity, organic or mineral, which may also be present. The presence of dissolved salts will accelerate or catalyse the corrosion due to these gases, but this action should not be confused with the corrosive effect of certain salts in the boiler and other units and which is due to their dissociation under boiler temperatures and pressures. *In the economisers the temperatures are not high enough to bring about the dissociation of these corrosive salts in the make-up; and, moreover, there can occur no concentration of these, since the water in any particular portion of the economiser tubes is being constantly and wholly changed.*

The condensate, which in many plants constitutes practically the whole of the boiler-feed, may also contain oxygen and carbon dioxide as well as other acids which have been generated in the boiler, and in cases where the make-up is small, any corrosion of the economiser tubes is chiefly attributable to these constituents in the condensate. Steel economiser tubes appear to suffer more severely from corrosion than do cast-iron tubes, frequently pitting very badly. The removal of scale-forming material from the make-up water may aggravate this corrosion, since, with all its disadvantages, a layer of scale in the tubes undoubtedly acts as a protection against corrosion. In modern plants, where the boiler-feed is almost pure condensate and the make-up but a few per cents., the water is practically free from scale-forming impurities, and hence the corrosive gases have free access to the bare metal of the economiser tubes. The protective nature of a thin layer of scale is generally recognised, and the artificial production of such has been suggested as an expedient to overcome the corrosion of brass condenser tubes. It is also interesting to note that cast-iron economiser tubes have often been found to corrode graphitically.

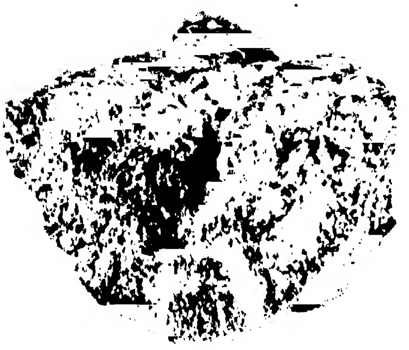

FIG. 13. HEAVY CARBONATE SCALE FROM ECONOMISER TUBE.

The scale deposited in economisers is usually a simple carbonate scale, for here again the prevailing temperature, whilst sufficient to decompose the bicarbonates of lime and magnesia and precipitate them as the normal carbonates, may not be sufficient, for instance, to throw down sulphate of lime. The solubility of this salt is reduced somewhat, it is true, but unless an excessive quantity is present in the water, its precipitation is unlikely. At 16° C. sulphate of lime is soluble to the extent of about 140 grains per gallon and at 100° C. to the extent of about 120 grains per gallon. It becomes dehydrated and insoluble at about 127° C. and normally, therefore, is not precipitated until it reaches the boiler. It should not be inferred, however, that this salt never occurs in economiser scale; it will be seen later how its presence may be ensured therein.

A considerable proportion of the bicarbonates may be decomposed and deposited in the economiser tubes, and in cases where the percentage of make-up is high and the make-up water bad, that is, impure, the tubes may become all but completely blocked with a porous carbonate scale. This state of affairs is well illustrated in fig. 13. This particular scale was removed from a three-inch economiser tube, and fortunately broke in such a way as to section itself longitudinally. The water channel was so narrow that it was barely possible to introduce a lead pencil into it. The composition of the scale was as follows:

Calcium carbonate	$CaCO_3$	65·41	per cent.	Carbonate content 92·45 per cent.
Magnesium carbonate	$MgCO_3$	27·04	,,	
Magnesia	MgO	2·28	,,	
Alumina	Al_2O_3	1·44	,,	
Silica	SiO_2	1·80	,,	
Ferric oxide	Fe_2O_3	0·20	,,	
Carbonaceous matter		1·30	,,	
Chloride	Cl	0·08	,,	
Calcium sulphate	$CaSO_4$	0·37	,,	
Moisture	H_2O	0·21	,,	
Undetermined	–	0·17	,,	

It is a typical carbonate scale, containing 92·45 per cent. of carbonate of lime and magnesia. The presence in it of free magnesia and calcium sulphate requires explanation. Carbonate scales are porous and are, therefore, permeable to the water. The thickness of this particular scale is so great, however, that considerable overheating of the economiser tubes must have taken place, and consequently the temperature, on the wider diameters of the scale, at any rate, must have been sufficiently high to decompose the precipitated magnesium carbonate into magnesium oxide, or hydroxide, and carbon dioxide (a decomposition which normally does not occur until the water reaches the boiler), and also to dehydrate and precipitate some sulphate of lime. It may also be observed that the ferric oxide content of the scale (0·20 per cent.) indicates that little or no actual corrosion of the tube has occurred. In fact, this quantity might readily have been introduced in the make-up itself. The protective action of the scale against the influence of a highly corrosive water is well illustrated by this example, the layer of scale in direct contact with the metal of the tube being baked to a hard and impermeable skin, which is quite different in appearance and is readily detached from, the bulk of the deposit, though there is little difference in composition, except with regard to the magnesia content, which is confined to this hard layer.

The carbon dioxide, liberated from the bicarbonates during the deposition of scale in the economisers, is carried forward by the water, together with any originally free dissolved carbon dioxide, and the dissolved oxygen which is given up by the water as bubbles of gas under the influence of the increased temperature. The corrosive influences of these gases are exhibited in the boilers, superheaters, and turbines, etc., or portions of them may be trapped in bends in the economiser tubes, where, unless relief taps are fitted in anticipation of this, severe local corrosion may be set up.

Corrosion of the external surfaces of economiser tubes is not so frequently met with, but it has been found to occur in cases where bad design or inefficient operation has resulted in abnormally low flue-gas temperatures. Under these conditions the sulphur dioxide and trioxide and carbon dioxide present in the flue gases set up corrosion on the tubes owing to the condensation of moisture which also occurs on them. A heavy deposit of scale on the inside of the tubes may, by causing overheating, lead to a rapid deterioration by simple burning.

Deposits from the flue gases, such as the acid sulphate of soda, originating from the fuel, can also cause very serious corrosion of the external surfaces of the tubes. A deposit of this salt is hygroscopic, and if, through leakage, low temperature of the flue gases or the access of moist air through inspection doors, etc., moisture condenses on the tubes, then the energetic corrosive action of the acid sulphate commences. A consideration of these possibilities may often explain the localised character of the corrosion whereby certain of the tubes only are affected, for example, the coolest tubes and those nearest to inspection doors. Tubes which are normally hot are not attacked by this deposit.

The formation of the acid sodium sulphate is supposed to occur by the combination of an excess of sulphur trioxide, produced from the sulphur present in the coal, and oxide of sodium, which latter has resulted from the decomposition of sodium salts, also present in the coal, by the incandescent carbon. The sodium oxide is volatile and is carried along by the furnace gases, together with the sulphur trioxide and condensed on the cooler surfaces as the acid salt, Na_2SO_4,SO_3 :–

$$(34)\quad Na_2O + 2SO_3 = Na_2SO_4,SO_3$$

The presence of moisture results in the production of the bisulphate of soda, and this, being an acid salt, gives an acid reaction in solution.

$$(35)\quad Na_2SO_4,SO_3 + H_2O = 2Na,H,SO_4$$

THE BOILER

In most technical processes which involve a sequence of operations, each performed by or carried out in a particular unit of the plant, there is one unit which may be regarded as the essential, the others being more or less refinements or additions made with a view to increased efficiency and economy. It is often the case that the essential unit is the one with which the greatest variety of troubles is experienced, and the boiler, as the essential unit of the steam-raising plant, is no exception to this. Excluding those due to bad design or manipulation and faulty material of construction, each variety of trouble is due solely to the impurities, solid or gaseous, contained in the feed-water. Even the burning and mechanical failure of plates and tubes which is usually attributed to external influences, such as the action of constituents of the fuel (as described in connection with economiser tubes), is an indirect or secondary effect of the feed-water impurities, being caused by excessive overheating resulting from the deposition of scale on the water side of the plates and tubes. Thus, if the overheating is so pronounced that a deposit of sulphate of soda, which we will assume to have been formed on the fire side of the metal, is fused, rapid oxidation of the metal will occur and a scale of magnetic oxide will be produced. Boiler conditions result in the scaling away of this oxide through frequent alternations in temperature and consequent contraction and expansion of the metal. The oxidation then recommences and a rapid weakening of the plate or tube is brought about, and bulging or "hogging" is the result which precedes complete breakdown. In the absence of water-scale and the accompanying overheating, the deposit of sodium sulphate has little or no harmful effect, since its fusion point is about 880 to 900° C., a temperature much above that to which the metal is normally raised. In the absence of moisture this salt is not corrosive. Hence, although this type of failure is generally ascribed to external influences, it is really brought about by the impurities in the feed-water.

In addition to scale or sludge deposition and corrosion, which are the two most serious troubles experienced in the boiler, there are the comparatively less serious ones, as "priming," "foaming," or "bumping," the development of leaks, the deformation or bulging of the tubes, and the evil effects accruing from the presence of oil or grease in the feed-water. The causes and nature of the latter will now be examined before proceeding to the more complex problems of corrosion and scale-formation.

Priming. Priming or foaming is due to the presence of certain impurities in the boiler water and is particularly troublesome when the working conditions are such that sudden and heavy demands are made for steam. When priming occurs, the bubbles of steam, instead of bursting when they reach the surface of the water, remain unbroken and form a froth or lather which may completely fill the steam space and be carried along through the steam pipes. It is essentially a condition of too free ebullition, and may be produced in several ways. The presence in the water of colloidal matter or of soap or other organic material will cause the water to froth when agitated, and the presence of much finely divided suspended matter results in an over-rapid liberation of steam by providing innumerable nuclei for the generation of steam bubbles. With these influences present, a steady steaming may often result in a kind of equilibrium in which the froth or foam, although produced, is not able to accumulate to the extent necessary for it to gain access to the steam pipes. If a sudden and heavy demand for steam is made, however, the resulting drop in pressure in the boiler is accompanied by a considerably accelerated rate of ebullition, and the froth is then carried forward through the steam pipes.

There is another, though less frequent, variety of priming, known as "bumping," and, as may be inferred from the term, it refers to explosive or intermittent boiling similar to that which occurs, for instance, when the load is suddenly increased, as just described It is caused by a superheated condition which is attained by the water, or in other words, by retarded ebullition. The phenomena is familiar in laboratory practice; solutions of caustic soda and of salts, if sufficiently concentrated, have, when heated, a marked tendency to remain quiescent and become superheated, and then commence to boil or "bump" so suddenly and violently that the large bubbles of steam which are formed reach the surface with such velocity as to throw the liquid out of the vessel. "Bumping" occurs in a boiler in a precisely similar manner. The effect of a concentrated alkaline water or of a concentrated salt solution, whereby a film of crystalline salt may be formed on the surface of the water, is to prevent the unrestricted formation and escape of steam, and the water may remain "stagnant" for a time. When sufficiently superheated, abnormally large steam bubbles are produced, not only on the metal heating surfaces, but also simultaneously throughout the mass of the liquid, and they escape so violently that they carry with them, not merely a spray of water, but an actual bulk of the liquid.

It is not usual nowadays that a sufficient concentration of alkali or salt is produced in the boilers to lead to priming, nor is it likely either that the saline content of the boiler water will reach a concentration at which a crystalline film is formed on the surface of the water. An oily scum has the same effect as either of these conditions, but here again modern practice considerably reduces the possibilities of the presence of a sufficiency of oil to ensure bumping, care being taken, for several reasons, to ensure that the boiler-feed contains as little oil or grease as possible. Probably the development of foaming or bumping into really serious troubles is chiefly confined to those boilers which drive engines which work intermittently, such as winding and similar machinery, and to cases of banks of boilers which contain one or more of a different type and having a much higher heat capacity. A sudden increase in load will cause these latter to prime. In these cases a quite moderate and ordinarily negligible tendency on the part of the water to prime is aggravated by the sudden application of "peak" loads, which, causing a drop in pressure, results in an instantaneous superheating of the water. Apart from the damage which might be caused by water entering the engine cylinders, perhaps the most serious source of danger which may arise through priming is the possible periodical and temporary emptying of certain of the tubes in a water-tube boiler. In this event there would be considerable risk of mechanical failure through overheating and burning.

The commoner causes of priming and like troubles in an up-to-date steam-raising plant are the sudden introduction into the boiler of finely divided suspended matter or the sudden formation of this kind of material in the boiler itself. Small quantities of suspended matter are probably useful in facilitating the free and uniform generation of steam bubbles, but larger quantities, particularly if of a light and flocculent nature, become "too much of a good thing" and should be avoided. Magnesium salts, when precipitated in a boiler, often form a very light and flocculent deposit, and this is one of the more frequent causes of priming troubles. This particular deposit occurs when magnesium salts predominate, as, for instance, may happen when the imperfect control of a softening plant has resulted in the removal of the lime salts but has not efficiently dealt with the more difficult removal or elimination of magnesium salts.

A badly controlled softening plant may also be responsible in other ways for priming. If the operation of the softener is irregular, the boiler water may contain permanent hardness, and consequently, when water containing an excess of soda comes along from the softener, there will be a sudden precipitation of the permanent hardness, which is equivalent to the introduction of innumerable fine particles. Priming therefore results. The reverse of this, viz., when unsoftened water is allowed to enter a boiler in which there is an excess of soda, has the same effect. The much-debated question as to whether sodium carbonate is in itself responsible for priming may well be explained in this way, as may also the somewhat common assertion that the installation of a softening plant synchronises with the development of priming troubles. The fact that, where sodium carbonate has been blamed for priming, this occurs intermittently, is strongly in favour of absolving the soda from blame, and it is very probable that, in the majority of cases, the trouble can be overcome by paying proper attention to the control of the softening plant. There is just one point, however, which should not be overlooked in connection with the installation of a softener to an already existing steam plant, in the boilers of which a scale may previously have been formed. The treated water has a softening and loosening effect on existent scale and may, in this way, lead to the production of sufficient suspended matter to develop priming troubles.

From the foregoing, the means of avoiding this class of boiler trouble are obvious: water-softening processes should be operated uniformly and should be designed to deal effectively with magnesium salts. If the make-up contains much suspended matter it may be necessary to filter it, or, at any rate, to resort to a judicious use of the blow-off cock. The proper time for blowing down is during those intervals when there is practically no demand for steam, for then the sediment has the best opportunity to settle and is more completely removed in consequence via the blow-off cock. When the boiler is under load, the suspended matter is fairly uniformly distributed throughout the bulk of the water, and under these conditions a blow-down of many inches is infinitely less efficient than a blow-down of even one inch during quiescent periods.

Other precautions against priming include the avoidance of excessive concentrations of saline material and of caustic soda (here also the blow-off cock is a useful instrument when properly applied), and the exclusion of oil or grease, especially those varieties which are saponifiable and which can produce soap in the boiler, either with alkali or alkaline-earth metal salts such as those of lime and magnesia. It is scarcely necessary to mention the provision of ample steam space in the boiler.

Troubles due to Grease or Oil. In common with the majority of boiler troubles, those due to the presence of oil or grease in the feed-water have forced themselves into prominence and have assumed a very serious character with the advent of high-pressure boilers and modern circulation systems. In the earlier days, when the make-up was 100 per cent. raw water, there was but little opportunity for oil to accumulate in the boilers, but with the present tendency to aim at a make-up of as nearly 100 per cent. condensate as possible, many facilities are given for oil and grease to gain access to the boilers. The damaging effects which oily feed-water may have on the boilers is now so thoroughly appreciated that insurance companies will not undertake the risk of insuring boilers which operate on such water. Condensed steam, *when properly treated*, is, of course, an ideal feed-water, both from the point of view of heat conservation and of its freedom from scale-forming and corrosive constituents, but these desirable qualities may be completely off-set if its oil content is not removed.

The influence of oil or grease is indicated primarily by a pronounced reduction in the evaporative efficiency of the boilers. In conjunction with scale, the overheating which the latter may induce is considerably accentuated, and bulging of the plates or tubes is caused. Sir A. J. Durston, K.C.B. (late Engineer-in-Chief to the British Navy), found by actual experiment that whilst the difference in temperature between clean plates and the boiler-water was 85° F., the difference between the water and plates covered with a greasy deposit, 1/16th of an inch thick, was 150° F., and that when this deposit of grease extended up the sides of the boiler, the temperature difference between the plates and the water was 537° F. He also states :

> "The results of experiments showed that a thin coating of grease deposited on the tubes during the ship's trials caused a loss in efficiency as heating surface, compared to perfectly clean tubes, of 8 to 15 per cent., the mean of many experiments giving 11 per cent."

C. E. Stromeyer, chief engineer to the Manchester Steam Users' Association, states also that—

> "A film of grease, one-hundredth of an inch thick, offers resistance to the passage of heat equal to a steel plate ten inches thick. In other words, grease offers one thousand times the resistance of steel to the passage of heat."

The reasons for this heat insulation are as yet speculative; one explanation is that the grease, by preventing actual contact between the water and the metal, restricts the transmission of heat to that by radiation only. Another suggestion is that the heat causes the film of grease to rise off the plates in the form of blisters which are filled with oil vapour or with superheated steam.

Whatever may be the actual reason, there is no doubt very small quantities of grease, either alone or together with scale, can give rise to bulging, and, further, if this occurs near seams, to actual leakage. When boilers are forced, as little as 0·1 per cent. of grease in a scale may result in the development of these troubles, and since the smaller the amount of scale the greater will be the proportion of grease in it, it should be remembered that the rather prevalent idea that a small quantity of grease is of no significance if the water is soft is a misapprehension, and that under such conditions the risks of excessive overheating are increased.

Scale and Corrosion.—When the feed-water enters the boiler, the dissolved gases together with the free carbonic acid resulting from the decomposition of the bicarbonates of lime and magnesia, and the volatile constituents or products from any organic matter which may be present, pass away with the steam and are largely, if not wholly, responsible for the corrosion which occurs in the steam spaces and superheaters, etc. The dissolved solids in the water, if permanently soluble, become increased in concentration, and the bicarbonates of lime and magnesia and the sulphate of lime are precipitated as scale or sludge.

Scales vary very considerably in composition, but they are generally classed as carbonate, sulphate, or silicate scales, according to nature of the predominating constituent. The carbonates of lime and magnesia are precipitated mainly as sludges, but in certain cases magnesium scales are formed and a certain proportion of the carbonate of lime is usually thrown down in a form which produces scale. Sulphate of lime is essentially a scale-forming constituent, and such scales are usually well characterised. They generally contain more or less calcium carbonate and magnesium carbonate or hydroxide, and the cementing property of the sulphate often results in the formation of a composite carbonate and sulphate scale by including the carbonate of lime when the latter is being simultaneously precipitated. In the presence of soluble silica, lime and magnesia may produce a silicate scale, probably the most destructive scale which can occur in a boiler. Carbonate scales, whilst decidedly disadvantageous, are the least destructive from the point of view of mechanical failure of the metal on which they are deposited. They are comparatively porous and therefore allow the boiler-water to permeate them, and for this reason do not normally induce such pronounced overheating of the plates and tubes as do the more compact scales. Also, they are less difficult to remove, and of the various water-treatments, that directed towards the elimination of the scale-forming bicarbonates is the simplest. The following is the analysis of a typical carbonate scale removed from a water-tube boiler:

Calcium carbonate	76·12 per cent.
Calcium sulphate	8·07 ,,
Magnesium carbonate	1·32 ,,
Magnesium hydrate	10·76 ,,
Ferric oxide	1·32 ,,
Water	2·43 ,,

Sulphate scales are harder and more compact, and cause overheating by restricting the transference of heat from the heating surfaces to the water. They are strongly adherent to the metal and are correspondingly difficult to remove. Silicate scales, consisting of silicate of lime or magnesia, or both, are even worse than the sulphate scales, and it is these two types which are generally responsible for the excessive overheating which leads to the bulging of the plates and tubes and the fusing of, and consequent corrosion by, furnace deposits on the fire side of the metal. Silicate scales are, however, much less common than are sulphate and carbonate scales. They may arise either through improper treatment of the boiler feed-water or from feed-waters which are naturally alkaline and which can dissolve considerable quantities of silica, given the opportunity.

Magnesium carbonate is precipitated from solution as such, but under boiler conditions it becomes converted into magnesium hydroxide, and free carbonic acid is evolved. This hydrate is very light and flocculent and is one source of priming troubles. If priming occurs, it is carried into the steam pipes and superheaters, and may, in cases of persistent priming, partially block up the tubes and even the steam spaces in the turbines. It may also become included in scales (see above example), although it does not itself form a scale unless the water is exceptionally dense or concentrated with respect to magnesium or sodium salts. Generally, however, when magnesium hydrate is present in large proportions in a scale it is cemented by sulphate of lime. Thus, in cases where the feed-water has been imperfectly softened, the more difficultly eliminated magnesium carbonate may be precipitated and compacted into a scale with the residual hardness due to sulphate of lime.

As already stated, calcium sulphate is essentially a scale-forming constituent. It is rarely found in sludge except in cases where its amount in the feed-water is relatively very small compared with the quantities of lime and magnesium carbonates. It is precipitated as the result of its dehydration, and is therefore always found in boiler scales as the anhydrous sulphate of lime.

Calcium sulphate scales and magnesium deposits may also be produced even when the feed-water originally contained the lime and magnesium in permanently soluble forms. Supposing, for example, the feed-water contains calcium nitrate and magnesium sulphate, neither of which is, alone, precipitated by boiling their solutions; inter-reaction will occur between them in the boiler and there will be produced the insoluble calcium sulphate, which appears as scale, and magnesium nitrate which remains in solution :

$$\text{(36)}\quad \underset{\text{soluble}}{Ca(NO_3)_2} + \underset{\text{soluble}}{MgSO_4} \qquad \underset{\text{insoluble}}{CaSO_4} + \underset{\text{soluble}}{Mg(NO_3)_2}$$

Of, if the feed contains calcium carbonate and magnesium nitrate, a similar exchange of acid radicles may take place and a portion at least of the magnesium will be deposited as the carbonate, or ultimately as the hydroxide, while a corresponding quantity of lime will remain in solution as the nitrate :

$$\text{(37)}\quad \underset{\text{insoluble}}{CaCO_3} + \underset{\text{soluble}}{Mg(NO_3)_2} \qquad \underset{\text{insoluble}}{MgCO_3} + \underset{\text{soluble}}{Ca(NO_3)_2}$$

It will be seen that, in this way, a hard sulphate of lime scale may be formed in a boiler even though the feed-water contained the lime in a permanently soluble form. In like manner, soluble magnesium salts may be acted upon to produce a magnesium sludge.

This type of reaction, involving an exchange of acid radicles, is responsible also for the formation of silicate scales. Normally, silica is soluble in water to the extent of about one-fifth of a grain per gallon. If the water is alkaline from any cause, either naturally occurring or through an excess of soda introduced in the softening process, then silica is dissolved by it much more readily in the form of sodium silicate, and if lime and magnesia are also present in the water, as may occur either in naturally alkaline waters or in cases where the softening process has imperfectly removed these constituents, then the silicates of lime and magnesia will be formed in the boiler and be deposited in the form of an extremely hard and strongly adherent scale. This kind of scale may also result from alkaline waters which contain suspended or colloidal clayey matter.

Other varieties of scale, of less frequent occurrence, are sodium sulphate and iron oxide scales. The former only occur, of course, when the boiler-water is allowed to become very concentrated, the solubility of this salt being presumably much reduced by the presence of other soluble salts. It is therefore thrown out of solution together with the other scale-forming constituents which are continuously being admitted in the feed or make-up. When actual corrosion of the boiler metal occurs, the corrosion products, instead of remaining as a loose deposit or sludge, may become incorporated, for instance, in a sulphate of lime scale, in which, however, the oxides of iron predominate. These scales result from acid feed-water or from the production of acidity in the boiler itself. As a matter of fact, very few boiler scales are entirely free from oxides of iron, showing that scale formation and corrosion can occur simultaneously or that corrosion may proceed underneath a scale. It is usually found, however, that after it has attained a certain thickness the scale arrests corrosion and in this respect acts as a protection to the boiler plates and tubes, and for this reason the oxides of iron are usually localised in the scale in a more or less well-defined stratum or layer.

When those constituents of the feed-water which participate in the formation of scale are precipitated, there remain in the water the soluble salts, both those occurring originally, and those which may have been produced by inter-reaction between two constituents as previously described. As the generation of steam proceeds the concentrations of the soluble salts increase. These may consist of sodium salts, the nitrates and chlorides of lime and magnesia and the sulphate of magnesia, and any or even all of these may occur in a boiler feed-water. Excluding for the moment the sodium salts, it is the presence and increasing concentration of the soluble constituents which is largely responsible for the rapid corrosion of the boiler plates, tubes, and fittings. In their absence, this corrosion can proceed by the action of the dissolved gases, oxygen and carbon dioxide, in the feed-water, but it is questionable as to whether these gases alone would result in such serious and rapid corrosion as that usually attributed to these soluble salts. The corrosion is often so violent that boiler plates, etc., have been known to fail mechanically through an excessive reduction in thickness in a much shorter time than experience would indicate as likely to result from the action of water and oxygen alone, or even if large quantities of carbonic acid were also present. The boiler is virtually a degasser, and the dissolved gases in the feed will be rapidly expelled by ebullition and carried forward by the steam. Thus the concentration of the dissolved gases in the boiler water may be reduced to and maintained at a very low figure, but their concentration in the steam represents practically the maximum for each specific case, and as a result, the corrosive influences of these gases is felt most severely in the subsequent units of the plant, the superheaters, turbines, and the economisers to which the gases are returned in the condensate. There may also be included the boiler steam spaces. Those portions of the boiler which are in contact with the water are situated, with respect to the rest of the plant, where the concentration of the gases is lowest, and it would seem improbable that any exceptionally violent corrosion occurring on them could be due to dissolved gas alone. It may be mentioned in this connection, that cases of severe localised corrosion have been attributed to the entrapping of these dissolved gases by angle irons and bends, etc., the remainder of the boiler being in good condition.

Of the soluble salts, magnesium chloride has the worst reputation from a corrosive point of view. It does not usually occur in natural waters in large amounts, but, as will be seen later, it may be produced in the boiler in considerable quantities. Even when present in the feed in small quantities only, its concentration in the boiler is constantly increasing, and any carbonate of lime, which is usually also present, and which, whilst in solution tends somewhat to hold the corrosive properties of the magnesium chloride in check, is soon precipitated as sludge or scale. Under boiler conditions of temperature and pressure the magnesium chloride is dissociated or decomposed, in contact with the iron plates and tubes, into its constituents, the nett result being the production of hydrochloric acid and magnesium hydroxide :—

$$(38)\quad MgCl_2 + 2H_2O = Mg(OH)_2 + 2HCl$$

The hydrochloric acid liberated in contact with the iron immediately attacks the latter to produce ferrous chloride :—

$$(39)\quad 2HCl + Fe = FeCl_2 + H_2$$

which is then acted upon by the magnesium hydroxide, produced as in equation (38), to yield ferrous oxide and to regenerate the original quantity of magnesium chloride. A corrosive cycle is thus established :—

$$(40)\quad FeCl_2 + Mg(OH)_2 = Fe(OH)_2 + MgCl_2$$

The amount of this corrosive salt is therefore not diminished as it exerts its destructive action, but as more and more feed-water is introduced and evaporated its concentration increases. For all practical purposes the magnesium chloride may be looked upon as a catalyst which accelerates the reaction :—

$$(41)\quad Fe + 2H_2O = Fe(OH)_2 + H_2$$

The greater its concentration, the more rapid is the resultant corrosion, and a point may be reached at which its dissociation is so rapid that a portion of the hydrochloric acid thereby produced is carried away by the steam and supplements the corrosive tendencies of the normally present constituents of the steam, gaseous oxygen, and carbon dioxide.

It will be seen that corrosion can occur in this way without the help of any free dissolved oxygen, and probably the chief function of this gas in such cases is to complete the oxidation of the metal commenced by the corrosive salt, by oxidising the black ferrous oxide to ferric oxide or rust. In doing this it will undoubtedly have an accelerating effect on the rate of corrosion. The ferric oxide in the presence of water is reduced by the underlying metallic iron to ferrous oxide and a second supplementary corrosive cycle is thus established :—

$$(42)\quad \begin{aligned} &(a)\ 4Fe(OH)_2 + 2H_2O + O_2 &&= 4Fe(OH)_3 \\ &(b)\ 4Fe(OH)_3 + 2Fe &&= 6Fe(OH)_2 \end{aligned}$$

In equation (39) it will be noted that hydrogen is liberated. The embrittling action of this gas on metal in which it is occluded is generally well known, and this factor very probably contributes towards the explanation of the premature mechanical failure of the metal.

Calcium chloride behaves in a similar manner to magnesium chloride. It is an unusual constituent of natural waters, but may be formed in the boiler if the water contains calcium carbonate and magnesium chloride. This is most likely to occur in marine sets when by some mischance sea water finds its way into the circulation system.

Magnesium chloride may also be formed by inter-reactions in the boiler. Natural waters invariably contain sodium chloride, and if magnesium sulphate is present in addition, the water virtually contains an equivalent amount of magnesium chloride, and should therefore be regarded as equally corrosive. The magnesium sulphate itself is corrosive, though less vigorously so than the chloride. On the other hand, the analogous case of a water containing calcium sulphate and sodium chloride cannot be looked upon as a calcium chloride, and therefore corrosive, water, since, unlike magnesium sulphate, the calcium sulphate becomes insoluble and is precipitated as scale. For the same reason the corrosivity of a water containing the soluble calcium chloride may be destroyed if sodium sulphate is present also, the calcium chloride being in this case precipitated as though it occurred originally as the sulphate. An equivalent amount of the sodium sulphate is, of course, replaced by sodium chloride.

The nitrates of lime and magnesium act corrosively in a similar manner to the chlorides, the cycle being represented as follows :—

$$(43)\quad \begin{aligned} &(a)\ Ca(NO_3)_2 + 2H_2O &&= Ca(OH)_2 + 2HNO_3 \\ &(b)\ 2HNO_3 + Fe &&= Fe(NO_3)_2 + H_2 \\ &(c)\ Ca(OH)_2 + Fe(NO_3)_2 &&= Fe(OH)_2 + Ca(NO_3)_2 \end{aligned}$$

Further reactions occur, however, due to the oxidising character of the alkaline-earth nitrates which oxidise the ferrous hydroxide, produced according to equation (43) (*c*), to rust proper, the nitrate itself being reduced at the same time to nitrite :—

$$(44)\quad 4Fe(OH)_2 + Ca(NO_3)_2 + 2H_2O = 4Fe(OH)_3 + Ca(NO_2)_2$$

A portion of the nitrate is also reduced to nitrite by the hydrogen liberated in equation (43) (*b*). Unlike the chlorides, therefore, the nitrates suffer a diminution in quantity by these reactions, and it is thought by some authorities that the above reductions proceed even further until the final products from calcium nitrate are calcium hydroxide and ammonia.

It is a common practice to test boiler water at frequent intervals for alkalinity, a positive result being considered as indicating a satisfactory condition of the water, since a slightly alkaline water is regarded as anti-corrosive. In the case of a water containing calcium nitrate, the free lime liberated as shown above may be responsible for a positive reaction being obtained on testing for alkalinity, and the boiler attendants may be deceived as to the true state of affairs in the boiler. The quantity of free lime necessary to answer to the alkalinity test is insufficient to counteract the corrosive tendencies of the water. Magnesium nitrate, on the other hand, is less likely to lead to this kind of deception, since the magnesia produced is less soluble than the lime and has therefore a less pronounced effect on the indicator used in testing. When tests for alkalinity are carried out as a routine procedure, steps should also be taken to make certain that the alkalinity is due to soda and not to lime. Moreover, as will be seen later, the soda alkalinity should preferably be caustic rather than carbonate. If, however, a complete analysis of the water shows that soluble calcium salts are absent and are not likely to be produced in the boiler, then a lime alkalinity is, of course, satisfactory.

Other corrosive salts which may gain access to the boilers are the sulphates of iron and aluminium and occasionally manganese. When iron is present in appreciable quantity it usually occurs as ferrous sulphate. The normal traces of iron are either in the form of ferrous oxide or bicarbonate, though the actual existence of the latter is extremely problematic. Ferrous sulphate, though soluble, is precipitated as basic carbonate or sulphate on exposure to the air and, as a result of this, the water containing it becomes decidedly acid. This precipitation and development of acidity will naturally proceed more rapidly in the boilers and the precipitated iron may form a sludge or become incorporated in a scale whilst the free acid "acts as usual." Sulphate of aluminium, which may originate from the alumino-ferric used in softening plants or from some other contamination, behaves similarly to ferrous sulphate, precipitating hydrated alumina and liberating free sulphuric acid. It is therefore equally as objectionable as iron salts and there may also be included in this category all ammonium salts, which dissociate into the free acids and ammonia, the latter being carried away in the steam as a volatile constituent. If present in any quantity, ammonium salts are practically equivalent to a direct pollution of the water with acid industrial effluents. The effect of sulphate of manganese is one which is difficult to estimate; it usually occurs together with iron and aluminium, and its individual influence is consequently masked, or obscured.

Sodium salts are always present in natural waters. Generally they are regarded as innocuous. They do not form scale unless, as already indicated, their concentration is allowed to considerably exceed the limits which are compatible with intelligent boiler practice, and they are not usually regarded as corrosive. The chloride, it is true, may be considered to be potentially corrosive when salts of magnesia are also present. The chief interest in sodium salts is centred about the carbonate, which, if present in quantity, causes the corrosion of the non-ferrous boiler fittings. Its behaviour under boiler conditions has recently received considerable attention, the first authority to draw public notice to this being Paul, who, in his book on *Boiler Chemistry and Feed-water Supplies*, devotes a complete chapter to its detailed consideration. Sodium carbonate undergoes decomposition in the boiler, producing caustic soda. Paul, however, gives very strong evidence in support of his theory that this decomposition is not a simple causticisation which would be accompanied by an evolution of carbon dioxide. Instead it is accompanied by an evolution of oxygen, as is indicated by the analyses of the condensates from boilers evaporating sodium carbonate waters. These show that whilst the oxygen content approaches the value representing saturation, the carbon dioxide content is rarely in excess of that which can be accounted for by the atmospheric carbon dioxide dissolved in the make-up or that arising from the decomposition of the scale-forming bicarbonates. Paul states :—

> " Four facts require to be carefully noted.
>
> (1) The destruction, partial or total, of the sodium carbonate.
>
> (2) The disappearance, partial or total, of the carbon dioxide. (From the causticisation of the sodium carbonate.)
>
> (3) The appearance of caustic soda in the boiler water.
>
> (4) The constant presence of oxygen in sufficient quantity to keep the condensed water nearly or quite saturated and also to escape with the gases from the air pump."

And continues :—

> " The presence of free oxygen may be ascribed to the make-up water which is often quite saturated with this gas, but, as in many cases the make-up is only 3 per cent. of the condensate (or total feed), and the condensate is always nearly or quite saturated, and in addition there is always an escape of air or gas containing oxygen, it appears more than probable that oxygen is a result of the disintegration of the sodium carbonate. The appearance of oxygen taken in conjunction with the disappearance of carbon dioxide and at the same time the formation of caustic soda, would point to a regrouping of the carbon and oxygen atoms."

By broadmindedly looking beyond the stereotyped classification of sodium carbonate as a mineral salt and regarding it as an organic salt or carbon compound, Paul has been able to advance a very reasonable and acceptable explanation as to the behaviour of sodium carbonate in modern high-pressure boilers.

The first stage in the decomposition of sodium carbonate is suggested to involve the formation of sodium formate and caustic soda :—

$$(45)\quad 2Na_2CO_3 + 2H_2O = 2H{\cdot}COONa + 2NaOH + O_2$$

The production of caustic soda and of oxygen and the *non*-production of carbon dioxide is in this way explained, and the supposition is substantiated by careful and original investigational work carried out by Paul. Very convincing evidence is offered with regard to the actual formation of sodium formate and also of other organic bodies in boiler waters which are concentrated in respect to sodium carbonate.

A carbonate water will not decolorise solutions of permanganate of potash, nor give positive results in tests designed to indicate the presence of organic compounds, such as sugars, for instance. After evaporation in a boiler, however, such water invariably answers to these tests. By referring back to the account of Paul's theory of the action of excess of carbon dioxide or carbonic acid on iron, a close analogy with the matter now being considered will be found, organic products being formed in each case. Experiments carried out by the author a few years ago, but which had, unfortunately, to be discontinued, also showed that if carbon dioxide is allowed to act in excess on pure iron suspended in pure water and excluded from contact with the atmosphere, the water after a time answered to all the common tests for the presence of organic compounds. Further, the products of the attack on the iron contained a considerable proportion of ferric oxide, indicating that some oxygen had been available to oxidise the first-formed ferrous oxide. The only possible sources of this oxygen were the water or the carbon dioxide, and as water alone, in the absence of oxygen, will not oxidise ferrous oxide, the only possible conclusion was that the oxygen must have been supplied from the carbon dioxide. If this is the case then the carbonic acid must have been decomposed in a manner similar to that suggested by Paul. On carefully eliminating the dissolved ferrous iron from the water in which the metal had been suspended, and then concentrating this water a syrupy solution was ultimately obtained.

Continuing with the decomposition of sodium carbonate, Paul's investigations indicated that this did not stop with the production of sodium formate, but that other reactions were induced. First there is the probable formation of sodium acetate from the formate :—

$$(46) \quad 2H{\cdot}COONa + H_2O = CH_3{\cdot}COONa + NaOH + O_2$$

Here, again, there occurs a liberation of free oxygen, and caustic soda is also produced. The next probable reaction is that which results in the production of acetaldehyde and the regeneration of sodium carbonate from the products of the first two reactions :

$$(47) \quad CH_3{\cdot}COONa + H{\cdot}COONa = Na_2CO_3 + CH_3{\cdot}CHO$$

The acetaldehyde, although volatile, readily polymerises or condenses into bodies of a sugary character, particularly in the presence of caustic soda, which latter may also react with the various products to form, for instance, acetone and lactic acid. It is fairly common knowledge that many boiler waters will give positive results when tested for the presence of sugars, and this somewhat mysterious fact may well be explained on the above lines.

This behaviour of sodium carbonate, when allowed to concentrate in high-pressure boilers, is therefore a complicated problem and, in addition to the fact that the non-ferrous boiler fittings are severely attacked, considerable significance attaches to the evolution of oxygen during the decompositions undergone by this salt. The effects of oxygen as a gaseous impurity in boiler feed-waters is becoming more and more universally appreciated, particularly with regard to the corrosion of the economisers, superheaters, and turbines.

THE SUPERHEATER

The function of the superheater is first of all to dry the steam and, secondly, of course, to increase its temperature. In the case of a boiler working at about 200 lb. per square inch pressure, the temperature of the dried and superheated steam is usually well above 500° F. Normally, therefore, the superheater tubes become coated with a skin of black or magnetic oxide of iron, Fe_3O_4. This coating is firmly adherent to the metal and after a time becomes sufficiently thick to protect the tubes from further attack by the dry steam.

Actual corrosion of superheater tubes is caused by the impurities in the steam, either gaseous (oxygen), volatile acids or material carried over from the boiler by priming. Such corrosion, however, is confined to the wet or inlet ends of the tubes and the inlet header. That is to say, it ceases when the steam becomes dry. In the absence of priming, the dissolved gases in the boiler-feed, together with those evolved in the boiler from saline impurities, are responsible for the corrosion in these units which is often exceptionally severe. Hydrochloric acid, produced in the boiler from the dissociation of magnesium chloride, either actual or potential, is a factor which will induce very rapid corrosion and is frequently indicated by the presence of chloride in the corrosion products, together with the absence of metals other than iron, showing that the chloride must have been carried over in a volatile or gaseous condition and not in solution as by priming.

When priming occurs, any sludge present in suspension in the boiler water is deposited in the super-heater tubes, and under exceptionally bad conditions may even accumulate to such an extent as to all but choke them. In addition, the soluble constituents of the boiler water are also deposited, so that there is left a mass representative of all the suspended and dissolved impurities in the boiler water. The behaviour of these in the superheater have, therefore, to be considered.

The carbonates of lime and magnesium are decomposed by the superheater temperatures, losing carbon dioxide and becoming transformed into free lime and free magnesia (not, of course, the hydrated oxides but the anhydrous oxides), some of which may be carried forward, in the form of a fine dust, by the rush of steam, to be finally trapped or deposited in some subsequent unit; for instance, the turbine. The rapid evaporation of the water, when primed over into the superheater, results in the deposition of the soluble constituents in a fine dust also, and these accompany the lime and magnesia in the steam current and are finally deposited with them. The following analysis of the corrosion products from superheater tubes illustrates the occurrence of free lime and magnesia and of other constituents of the boiler water. Priming has occurred, but not to a serious extent :—

Lime	CaO	1·65 per cent.
Magnesia	MgO	1·58 ,,
Calcium sulphate	$CaSO_4$	0·87 ,,
Sodium chloride	$NaCl$	2·11 ,,
Free carbon	C	2·14 ,,
Silica	SiO_2	1·55 ,,
Ferrous oxide	FeO	6·40 ,,
Ferric oxide	Fe_2O_3	83·68 ,,
Phosphoric acid	P_2O_5	0·07 ,,

Other salts, such as the nitrates, decompose in the superheater, producing the corresponding acid anhydrides and the anhydrous oxides of the metals. Magnesium nitrate in the boiler dissociates into hydrated magnesia and nitric acid (see equation 43) but in the superheater the acid exists as N_2O_5 and the magnesia as MgO. So long as the steam is wet, the acid anhydrides will be present dissolved in the moisture and behave as the acid proper, causing corrosion, but when the steam is dried and moisture, as a result, absent, they are innocuous. For this reason the wet ends of the superheaters are attacked whilst the tubes further on escape. The effect of these acid anhydrides on the corrosive properties of the steam if the latter becomes wet requires no further comment.

THE TURBINE

If corrosion occurs in the turbine it is analogous in character to that which takes place in the superheaters. It is due primarily to dissolved oxygen originating from the boiler-feed and secondarily to any volatile acidity which may be generated in the boiler. Further, as in the superheaters, the corrosion which occurs during running periods, and which is usually more violent than that which may take place during shut-down periods, is confined to those stages of the machine in which the steam is wet, and may be accelerated by the deposition of salts carried over from the boilers, via the superheaters, by priming. The following is an example of an exceptionally heavy deposit which was found adhering to the blades of a turbine, in quantities which seriously restricted the steam passages :—

Calcium carbonate	43·20 per cent.
Calcium sulphate	4·29 ,,
Lime	4·33 ,,
Magnesia	4·51 ,,
Sodium chloride	0·45 ,,
Silica	5·74 ,,
Alumina	2·81 ,,
Ferric oxide	17·06 ,,
Ferrous oxide	1·17 ,,
Oil	16·56 ,,

This deposit appeared as a pasty mass cemented by the oil, and suggests that considerable priming has occurred in the boilers. In this particular case, little or no corrosion of the blading had taken place, but this is explained by the presence of a large percentage of alkali carbonate and of oil, especially as the presence of chloride assists corrosion. When corrosion pure and simple occurs, the products are composed of ferrous and ferric oxides, but it is seldom that chlorides, even though in very small traces, are absent, and the catalytic effect of these on the wet oxidation of ferrous material is generally well known. The following is a typical analysis of the corrosion products from the blades of a turbine in which corrosion has been due entirely to oxygen in the steam :-

Ferric oxide	81·24 per cent.
Ferrous oxide	18·13 ,,
Silica	0·32 ,,
Sulphate	0·12 ,,
Phosphate	0·17 ,,
Chloride	trace ,

The disposition of the corrosion which may occur in turbines during running periods is of interest. It is invariably found that the blades on the high pressure stages of machines fed with superheated steam are quite free from corrosion but are covered with an adherent layer of black magnetic oxide. The number of stages so affected corresponds with that portion of the machine in which the steam is superheated and dry. As soon as the steam loses its superheat and becomes wet, corrosion may commence and hence may make its appearance somewhat abruptly on a particular and well-defined stage. Following on this the next two or three stages suffer the most severely, but then, as the low-pressure end of the turbine is approached, the violence of the attack, as evidenced by the condition of the blades, becomes more and more reduced, and it is not uncommon to find the blades on the last stage in almost as good condition as the magnetic oxide-coated blades on the high-pressure stages.

Roughly speaking, then, it is the middle stages of the turbine which, if corrosion occurs, suffer most during running periods, and in view of the fact that oxygen, and, in certain cases, other constituents of the steam, are responsible for this, the reasons are not difficult to find. At the point where moisture is first formed in the steam, the concentration of oxygen in the latter is, relative to other points along the machine, at a maximum, since no corrosion has occurred on previous stages to reduce it. Also, the concentration of water in the steam is at its lowest, and the pressure, relative to subsequent stages, is high. Consequently the concentration of oxygen dissolved in this first small quantity of water also represents a maximum value, and we have seen earlier that the rate of corrosion is directly proportional to the amount of dissolved oxygen in the water. In addition, the temperature at this point of the initiation of corrosion is higher than on succeeding stages. As the low-pressure end of the turbine is approached, the amount of water in the steam increases, the pressure decreases and the quantity of oxygen decreases owing to its partial exhaustion by corrosion on previous stages. Therefore the concentration of this gas in the water is reduced and the rate of corrosion becomes decreasingly rapid. The progressive fall in temperature is, of course, another retarding factor.

The corrosion which may occur during standing periods is generally of little consequence, since the precautions necessary to safeguard against this are fairly common knowledge and are usually adopted. Such corrosion, however, is due to the condensation of moisture on the blades, etc., as through leaky or imperfectly closed steam valves, and to the access of atmospheric oxygen. It will attack the blades on each stage more or less uniformly with the exception of those on which a coating of magnetic oxide has been produced during running. In any case it is unusual that machines are shut down for sufficiently long periods for this type of corrosion to proceed very far at a time, and it is generally admitted that the progress of serious deterioration of the blading occurs whilst the machine is running. Nevertheless, unsatisfactory standing conditions frequently initiate corrosion and therefore in cases may be largely responsible for it.

CHAPTER IX

THE CORROSION OF CONDENSER TUBES

THE problem of the corrosion of condenser tubes, *i.e.* of brass, is one whose full discussion would require as much space as that of the corrosion of ferrous materials. For many years the extension of knowledge with regard to the corrosion of copper alloys was very slow, due, no doubt, to the fact that, although it is a matter of very considerable importance to Power-house and Ship's economy, it comprises but a part of the general corrosion problem, a part which is relatively of minor financial significance. During recent years, however, the wastage resulting from the frequent and rapid deterioration of condenser tubes and the consequent failure of the condensers, has stimulated investigation into the causes, mechanism and the means of preventing their corrosion and a large amount of literature has accumulated which records the results and experiences of different workers, their observations, theories, and conclusions. The subject is still in an immature stage of development compared with that of the corrosion of iron, differences in opinion are wider and more common, and theories exist which, although very capably exploited, are based on hypotheses which are extremely improbable. The incompleteness of the knowledge acquired is well illustrated by the fact that it is frequently impossible to offer a satisfactory explanation of a particular case of condenser tube failure, or why, in one condenser, an occasional tube will fail, rapidly and completely, whilst the remainder show little, if any, signs of having been in service.

Generally speaking, most of the factors which are operative in the corrosion of iron are similarly operative in the corrosion of brass. In the first place, there may be observed the same three main types of corrosion:—

(1) Auto corrosion.
(2) Contact corrosion.
(3) Externally induced corrosion.

The first type results when the brass is in contact with an electrolyte but is not in contact with any conducting solid: the second type when, in addition to being wetted by an electrolyte, the brass is also in contact with some other solid conductor, either metallic or non-metallic, and the third type when the brass serves anodically for an externally generated E.M.F.

Secondly, there are two main forms in which the corrosion of brass may exhibit itself: (1) where both the constituent metals are dissolved or removed at the same rate and in which the corrosion products contain zinc and copper in the same proportions as those in which they exist in the original metal—this is, of course, uniform corrosion, and the deterioration assumes the form of a general thinning of the tube walls; (2) where a preferential attack on one of the constituents of the brass occurs, it may be either on the zinc, resulting in the so-called dezincification of the brass, or on the copper. This latter form is comparable to the pitting of ferrous material and, similarly to pitting, causes a more rapid breakdown of the tube. This case may also be extended to include the results of the simultaneous solution of both constituents, but in which one of them, the zinc, is removed at a greater rate than the other. The pitting may, therefore, appear actually as such, or may be represented by portions of the tube in which the material, residual after the removal of one constituent, is devoid of mechanical strength, *i.e.*, spongy copper.

Thirdly, the processes of corrosion are electro-chemical ones, and the presence of liquid water is therefore essential. Also, the following factors each have their influence on the corrosion:

(1) Aëration of the water.
(2) The saline concentration in the water.
(3) The action (catalytic) of the products of corrosion.
(4) The temperature.
(5) The composition of the alloy.
(6) The physical condition of the alloy.

As in the case of iron, if the water contains no oxygen, corrosion does not occur, initial attack may occur, but soon ceases through lack of oxygen, which, according to some authorities, acts primarily as a depolariser and, to others, by converting protective products into stimulative ones. When oxygen is present, corrosion takes place, and there may occur dezincification or the selective solution of the zinc, removal of both the zinc and the copper in which no residual free copper is left, or removal of both the zinc and the copper, in which, in addition to the formation of copper products, there is left a quantity of residual, metallic, spongy copper. At ordinary temperatures, the attack on the brass increases with the extent of aëration, and this also appears to increase the proportion of zinc in the corrosion products. It is interesting to note that the corrosion of copper alone in sea water is retarded by aëration, due probably to the formation of a protective film of oxide, whilst the corrosion of zinc alone in sea water is accelerated by aëration.

Increases in temperature up to about 50° C. increase the rate of corrosion, after which the rate falls off; it is less at 60° C. than at 30° C. According to Gibbs (*Trans. Faraday Soc.*, **11**, 1915 1916) the attack in sea-water takes place in three successive stages. First there is a slightly preferential solution of the copper, then a period during which both the zinc and the copper dissolve or are removed at approximately equal rates, and finally an increasingly selective solution of the zinc. That is to say, during the first stages the copper is removed more rapidly than the zinc, but the rate of solution of the zinc continually increases and for a time is about equal to that of the copper, after which the zinc maintains a higher rate of solution than the copper.

He also states that this latter condition is reached more quickly in stagnant water at 15° C. than at 50° C. and is probably dependent upon the amount of oxygen and carbon dioxide dissolved in the water, being hastened by aëration and apparently associated with the production of a film of copper oxide which protects the copper, but which does not prevent the solution of the zinc.

Changes in the relative rates of solution of the constituent metals of 70/30 brass are also occasioned by variations in the saline concentration of the electrolyte. In diluted sea water the rate of corrosion, as a whole, is slower than in neat sea water, but the proportion of zinc in the products of the attack is higher and increases with increasing dilution. Gibbs records that after 34 days at 50° C. in gently aërated sea water of the following concentrations:

$$\frac{N}{1},\quad \frac{N}{2},\quad \frac{N}{4},\quad \frac{N}{8},\quad \frac{N}{16}$$

the percentage of zinc in the corrosion products was respectively as follows:

18·0 24·2 33·9 44·1 58·5

A constant increase in the relative rate of the solution of the zinc is therefore exhibited, and this is in line with the frequently observed fact that estuarine waters are more selectively corrosive than is neat sea water, and are more conducive to dezincification. This may be facilitated by the increased solubility of oxygen and carbon dioxide in diluted sea water, the carbon dioxide content increasing the attack on the zinc and the oxygen content retarding the solution of the copper, the solubility of which in gently aërated sea water is progressively reduced by dilution.

Of the products formed during the corrosion of brass, those which appear to act as stimulative agents in the subsequent attack are the oxy chlorides; the copper oxy-chloride catalytically accelerates the removal of the copper and the zinc oxy-chloride of the zinc. The formation of these salts, which may or may not be direct, depend upon other general conditions; thus, the copper salt may be produced at ordinary temperatures and the zinc salt at higher temperatures.

The chemical composition, the presence of other metals such as tin and lead, structural and physical heterogeneity, and the presence of embedded impurities, all have influences more or less comparable with those obtaining in the case of iron. A homogeneous α-brass corrodes as a rule more uniformly than a brass containing the α- and β-phases which is the more susceptible to selective attack or non-uniform corrosion. Cold-worked material is also more liable to attack, and this is more rapid at those points which mark the inclusion of foreign matter, as in rolled material, etc.

Notwithstanding this general similarity between the corrosion of ferrous and cuprous material, the latter has many distinctive features, however, and is particularly complicated, and for those who wish for a detailed account of the researches, etc., which have been made in this connection, the list of references, given at the end of this chapter, may be of use. The remainder of the space available will be devoted to a reproduction of what must be regarded as "the most up-to-date and authoritative expression of opinion" on the problem of the corrosion and protection of condenser tubes. In 1910 a committee, The Corrosion Research Committee, was founded by the Institute of Metals, and it represents probably the first organised campaign of investigation into corrosion problems to be instituted. The results of ten years' research and practical experience are embodied in a pamphlet, *Notes on the Corrosion and Protection of Condenser Tubes*, by G. D. Bengough, M.A., D.Sc., which, through the courtesy of the Institute of Metals, by whom it was published in 1922, the author is able to include :—

" The general use of brass for condenser tubes appears to have arisen as a reasonable compromise between the three factors of (*a*) suitable mechanical properties, (*b*) low corrodibility, and (*c*) moderate cost. It is comparatively easy to meet two out of these three requirements, and brass has in the past given a fair approximation to all three. The increased trouble caused by its occasional failure under certain conditions in recent years made it desirable to ascertain the causes of the corrosive action which brought about failure, and these causes have now been fairly fully elucidated. The question of improving the resistance of the tubes to corrosion has also been taken up, and several entirely different methods of doing this have been investigated. This part of the work is not yet finished. The notes give an outline of the present position, and indicate the lines upon which the work is now proceeding.

" The subject of corrosion of condenser tubes is a particularly complicated one, because it is closely concerned with three types of factors, namely :—

" (*a*) Very involved chemical and electro-chemical reactions which vary with different types of water, temperature conditions, time, etc.

" (*b*) Engineering conditions which are difficult to elucidate, such as the conditions of flow of water in the tubes, pipes, water-ends, etc., and the formation of froths and foams.

" (*c*) Metallurgical factors, such as the grain size of tubes, the presence of intercrystalline lines of preferential attack, and the existence of surface layers, on cold-worked metals, which behave differently from the underlying material.

" Thus it happens frequently that a case of corrosion cannot be attributed to any one single cause. Serious corrosion is usually the final net result of a number of factors working together, and these factors may be included in either or all of the three types (*a*), (*b*), and (*c*). The nature and the effectiveness of each factor are unlikely to be the same in any two cases of corrosion occurring in different condensers. Indeed, it has been found that the conditions, chemical and physical, are far from uniform even in a single condenser tube. Lists of factors which may affect corrosion are given later, and will be discussed in some detail. These lists contain the gist of what is known at the present time. Sufficient knowledge for a complete understanding of some types of corrosion problem is still lacking in all three branches of the subject, but the present notes are intended to give a general account of existing knowledge.

" The usual practice of to-day is for condensing-plant makers to specify 70/30 brass or 70/29/1 alloy for sea-water conditions, or where known corrosion has taken place, except in a few cases in which a consulting engineer or a chief electrical engineer of a power station, or a marine superintendent, specifies a mixture from his previous experience.

"This practice relieves the tube-maker of the responsibility of choosing a tube mixture for any particular conditions, a responsibility he is no doubt glad to avoid, but it occasionally results in a somewhat unsatisfactory state of affairs.

"It happens frequently that the tubes specified of one of the usual compositions will inevitably corrode in the conditions in which they will be placed. In due course the tubes fail, and the user claims satisfaction from the maker, as the cause of the trouble is actually unknown to him, but appears to be due to some fault in the alloy. The maker may then reply that the tube is as specified, and a deadlock results.

"Sometimes the case superficially appears to be very strong against the maker, particularly when a tube shows what is commonly known as 'dezincification.' In such cases the user may point to coppery spots in the tube, and claim that their occurrence is clear proof that the metal was badly mixed in the crucible and that the tube should be replaced.

"It is necessary, therefore, to state that it has been fully proved that the occurrence of such coppery spots in tubes is not dependent on good or bad mixing of the copper and zinc in the crucible. Such coppery spots are the result of purely corrosive action, the copper being redeposited from solution. Such action may occur in the purest and most carefully manufactured 70/30 brass and Admiralty alloy tubes it is possible to produce, provided that the tubes are subjected to certain corrosive conditions. (The presence of a trace of arsenic in the tube will prevent the formation of these copper spots, but it is not certain that the life of the tube is prolonged in consequence. In certain cases the contrary appears to be the case.)

"The trouble, in fact, must be attributed to conditions external to the tube and not to the tube itself. This, however, is not to say that all tubes are good, and they may, in fact, suffer from defects which render them unsuitable for use in condensers.

"It is necessary, therefore, first to distinguish between those causes of trouble which can fairly be held to be due to the tubes and those which are due to the conditions in which they are placed, and then to consider what measures can be taken to palliate such troubles. The fact must be emphasised, however, that if a tube of a particular composition is used in conditions unsuitable to that mixture, no absolutely certain means of preventing corrosion of the tube is available at present. Under certain sets of conditions a tube different in composition from those now commonly in use is desirable, and search for it is now being made.

"The causes of tube failure are classified below under two heads--viz. (1) causes which are due to the tubes and (2) causes which are due to conditions external to the tubes.

"(1) *Causes due to the tubes.*

- "(*a*) Laminations, spills, etc.
- "(*b*) Faulty composition.

" (*c*) Unsuitable crystalline structure.
" (*d*) Mechanical failure, *e.g.*, collapse under packing, splitting, season cracking, etc.

" (2) *Causes due to external conditions.*

" (*e*) Local accumulation of corrosion products.
" (*f*) Settling of foreign substances on the tubes; sometimes giving rise to (*e*).
" (*g*) Subsidiary supplies of steam entering condenser apart from main, giving high local temperature, and, sometimes, external erosion.
" (*h*) Inlet deterioration on upper internal surface of tube.
" (*j*) Electrical leaks and thermo-electric action.
" (*k*) Water speed, especially with dirty inlet water, as in certain harbours and docks.
" (*l*) Entrance into certain waterways, especially when tubes are new, *e.g.* Ship Canal and certain tropical rivers; certain docks; the Tyne at certain periods of the year; the upper reaches of the Clyde.
" (*m*) Air sucking due to rolling in bad weather, air leaks in pump line, etc.
" (*n*) Unsuitable design of water-end.
" (*o*) Ferrule troubles.
" (*p*) Too high a temperature.
" (*q*) The presence on new tubes of certain iron compounds.
" (*r*) Short-circuiting of contaminated cooling water.
" (*s*) Seasonal and other variations in water composition.

" Except in rare cases, corrosion takes place on the inner (*i.e.* the water) side of the tubes, and in practice it usually happens that the factors (*e*) to (*s*) are not under direct control of the engineers in charge. Frequently the cause of failure is not a single item in these lists, but two, three, or more working together. The corrosion which results from the causes tabulated above may take one or two forms to which the following names have been applied :

" (1) 'Complete corrosion'; *i.e.*, both copper and zinc are attacked, and either removed in solution or converted into basic salts.
" (2) 'Selective action' or 'dezincification'; apparently only the zinc is attacked, and the copper left *in situ*.

" What is commonly called 'complete corrosion' is usually characterised by the presence on the inner surface of the tube of much blue-green basic copper salt, which colours the white salt of zinc, and of red cuprous oxide. As a matter of fact, both types of action are really complete corrosion, since both copper and zinc are attacked.

" What is called 'selective action' or dezincification is usually characterised by a white salt of zinc overlying considerable deposits of metallic copper. This copper is generally supposed to be either unalloyed copper lumps, or else unattacked copper which was originally present in the alloy from which the zinc has been removed by electrolytic action. Neither of these views is correct. Both the copper and the zinc originally present in the alloy have been attacked by the initial corrosive action, and the copper has really been redeposited from the copper chloride so formed. The term 'dezincification' is therefore misleading and might well be abandoned.

"It sometimes happens that metallic copper and white zinc salt, which are usually characteristic of the one type of action, and cuprous oxide and the blue basic copper salt, which are characteristic of the other type, are all found together as the result of corrosive action. As a matter of fact, no sharp line can be drawn to separate the two types of action. They fade into one another through intermediate types in accordance with the prevailing chemical and physical conditions. Such differences as there are between the extreme examples are concerned with the final products of corrosion, and not necessarily with the initial action. These differences are due to variations in secondary or tertiary reactions, which in turn depend on the local chemical conditions external to the tube, such as temperature, or to the presence of certain subsidiary metals present in the tube itself, such as arsenic and iron.

"It should be borne in mind that the occurrence of deposited copper on a corroded tube is not necessarily a sign that the tube is inferior to one that has not corroded in that particular way. The deposited copper sometimes forms a fairly coherent mass, but is not watertight or strong enough for use when there is no longer any backing of unchanged brass to support it; nevertheless, it may serve a useful purpose in hindering the rate at which oxygen can reach the still unchanged brass. Sometimes the action is so slow that the tubes last over twelve years before complete perforation by local or general leakage.

"The causes of corrosion which are due to the tubes themselves will now be considered in order:–

"(*a*) LAMINATIONS AND SPILLS

"These are formed in the tubes during the drawing process, and are not in themselves initiating causes of local action, but if corrosion starts from other causes, the metal of the tube is more liable to become disintegrated in the neighbourhood of the flaws than elsewhere. This is due to exfoliation or mechanical flaking away of the metal of the tube, and leaks may eventually occur, owing to the thinning of the tube walls in this way. W. Ramsay (*Engineering*, July 13, 1917) considers this action an important cause of tube failure, but in the present author's experience it is very rare for tubes to fail from this cause.

"(*b*) FAULTY COMPOSITION

"As regards composition, a fair specification for an ordinary 70/30 brass tube would be copper not less than 69·5 per cent., nor more than 71 per cent., and the zinc not more than 30 per cent.: other metals, unless added intentionally, should not exceed 0·4 per cent. Such other metals which may be found in brass tubes are lead, tin, iron, and sometimes nickel, manganese, aluminium, and arsenic.

"If the tube be made of cathode copper and electrolytic zinc, the tin is usually less than 0·1 per cent., but if B.S. copper and ordinary spelter are used it is occasionally as high as 0·25 per cent. Such small amounts of tin are not known to have any special effect on the behaviour of the tube as regards corrosion. The proportion of lead which occurs in tubes made of cathode copper and electrolytic zinc should be below 0·1 per cent.; with ordinary spelter and B.S. copper it may be as high as 0·25 per cent. One well-known firm considers it advisable to introduce nearly 2 per cent. of lead into condenser tubes, giving an approximate composition of 70 per cent. copper, 28 per cent. zinc and 2 per cent. lead. The object of this is considered to be to take advantage of the protective action of certain basic salts formed from the lead. Such tubes have behaved better than 70/30 tubes under certain estuarine conditions: in sea-water conditions the presence of lead does not ensure freedom from the white salt type of attack (*i.e.* 'dezincification').

"As regards the iron, the tube if made from electrolytic copper and zinc should not contain more than 0·1 per cent. In ordinary tubes, however, as much as 0·25 per cent. and even 0·35 per cent. is not infrequently found; occasionally 0·5 per cent. is reported. This metal is undoubtedly the most harmful of the common impurities, and greatly enhances the rapidity of the white salt attack in sea and estuarine waters. It is desirable that all specifications should contain an agreed limit as to the amount of iron the tube may contain, the permissible amount depending on the nature of the circulating water. (In hard fresh water, such as London waters, the presence of iron is much less harmful than in the case of sea water; in the latter case and in estuarine waters it should be kept as low as possible, *i.e.*, below 0·1 per cent.)

"Manganese is only occasionally found in tubes in determinable quantities, unless it has been added intentionally. In the latter case as much as 0·8 to 1·0 per cent. may be introduced, but this has not hitherto been found to confer any conspicuous advantage on the tube in resisting corrosion. The small amounts which are occasionally found under the former head do not usually amount to more than 0·05 per cent.

"Nickel in small quantity does no apparent harm, but aluminium should be rigorously excluded.

"Admiralty tubes contain 1·0 per cent. of tin instead of 1·0 per cent. of the zinc, that is, they consist of 70 per cent. copper, 29 per cent. zinc, and 1·0 per cent. tin. These tubes resist the white salt attack longer than tubes which do not contain more than a trace of tin, and under conditions in which the vacuum in the condenser will be less than 28½ inches (and consequently the maximum temperature may be over 30° C.). Admiralty composition should always be specified in preference to the plain 70/30 brass, except with waters known to be only slightly corrosive.

"(c) UNSUITABLE CRYSTALLINE STRUCTURE

"There is evidence to show that 70/30 brass and Admiralty tubes which have had their structures 'refined' by annealing at a temperature in the neighbourhood of 350° C., so that recrystallisation has occurred but crystal growth has been slight, are more resistant to corrosion than tubes which have not been so treated, and which, consequently, have a coarser structure. This treatment was originally proposed by Shaw Sparrow, and there is no doubt that occasionally coarse structured tubes are liable to an intercrystalline corrosive attack that may cause considerable trouble.

"When specifying brass tubes, it is therefore advisable to call for a final annealing treatment, *i.e.*, subsequent to the drawing processes, in the temperature range 350 ± 25° C. in an oxidising atmosphere. Such treatment has but a trifling effect as regards softening the tube, and does not interfere with the making of a tight joint at the ferrule. Tubes so treated have a fine crystalline structure. They must not be pickled after the final annealing. In bad conditions, however, this low temperature annealing will not *prevent* corrosion, but only retard it to some extent. Nevertheless, the process, which adds but a trifle to the cost of the tube, seems worth a more extensive trial than it has had at present.

"(*d*) MECHANICAL FAILURE

"This may be due to the fact that a tube is either too hard or too soft, owing to its treatment in the drawing shop. In the former case it is liable to fail by splitting, and in the latter case by collapsing when screwed up for packing purposes. A collapsed tube which bulges inwards is more liable to corrosion in the neighbourhood of the ferrule than is one which has retained its original shape. A detailed discussion of mechanical failures, such as season cracking, etc., is outside the scope of these notes.

"Failures Due to External Conditions

"(*e*) THE LOCAL ACCUMULATION OF CORROSION PRODUCTS

"It has been found that the salts formed when copper or brass is corroded by sea water are complicated mixtures, some of the constituents of which are harmful, some neutral, and some even protective. If, therefore, these products accumulate on, and stick to, the tube, instead of being swept away in a stream of circulating water, the tube may be either locally protected or locally corroded, and there is thus always a chance that local corrosive action may take place, and this type of action is one of the most frequent causes of corrosion, as well as one of the most difficult to control. The chemical changes involved are somewhat complicated, but it may be said that an active corrosive agent is colloidal cuprous chloride which changes in part to cupric chloride, a substance which rapidly attacks either copper or brass. It is clear that an attack due to salt accumulations is purely a matter of chance, and is beyond the control of either the tube manufacturer or the engineer in charge of the condenser. The possibility of it is inherent in the types of tube at present employed. As an instance of attack by corrosion products the well-known effect of preferential attack at a water-line is an example. This is mainly dependent upon the nature and distribution of the products of corrosion, and is not, as is usually supposed, due principally to the depolarising action of the air. Under certain conditions the products of corrosion may give rise to 'concentration cells' which may give rise to very rapid pitting.

"(*f*) SETTLING OF FOREIGN SUBSTANCES ON THE TUBES

"Many types of foreign substances may obtain entrance into a condenser and may settle on the tubes; the majority of such substances, *e.g.*, sand, clinker, wood, weed, etc., are chemically harmless in themselves. They may, however, exert indirectly a very harmful action on the new tubes, owing to the fact that they give a focus for the collection of harmful products of corrosion; some foreign bodies, such as hydroxide and other gels, which have been precipitated from colloidal solution, have absorptive properties which may cause considerable trouble, but this branch of the subject is too complicated for detailed discussion here.

"It is clear, again, that this type of corrosive attack on a tube is not under the control of either the tube manufacturer or the engineer; for instance, a passing ship may stir up mud, slime, sewage, etc., and cause it to be sucked into the condenser inlet of a ship or estuarine power-station and deposited on the tube surface, and thereby cause corrosion. The danger is greatest with new tubes; after certain types of scale have formed on tubes there is less danger from this source.

"(g) SUBSIDIARY STEAM SUPPLIES ENTERING LOWER PART OF CONDENSER

"An occasional cause of trouble in condensers is the introduction of subsidiary steam supplies into the lower part of the condenser, and the direct impingement on the colder tubes in the condenser of the steam. The result is that the tubes opposite the steam inlet show erosion on the outside, and sometimes also local 'dezincification' or white-salt attack on the inside, even when tubes containing 1 per cent. of tin are used, and rapid failure results. Failure may be due either solely to erosion from the outside of the tube, or the main trouble may be corrosion from the inside accelerated by high temperature, erosion being a contributory factor. Erosion may be pronounced with quite low steam pressures, such as 12 or 15 lb. (Expansion from several pounds pressure to a high vacuum gives rise to considerable increase in velocity, and probably the erosion is caused by suspended solid particles and water globules colliding with the tube at high speed.) All auxiliary steam should be led into condensers at the top with the main steam, and as far from the tubes as possible.

"(*h*) TOP INLET DETERIORATION

"A fairly common form of deterioration of condenser tubes is one that occurs at the inlet end at distances from 1 to 4 inches from the end of the tube. It usually occurs on the top and sides of the tube, but is occasionally also found on the bottom, and the tube is rapidly worn away in an irregular manner. This type of attack is due to the local formation of a 'foam clot,' a matter which is dealt with below.

It is sometimes aided by the erosive action of solid particles entering the water end in suspension, and by 'water-hammer' action.

"(*j*) ELECTRICAL LEAKS

"These may possibly be the cause of corrosion; such action, if it takes place at all, will be found to occur at and near one of the ends of the tube, and will not spread far into it. It is not probable that this is a frequent cause of trouble.

"(*k*) WATER SPEED

"The effect of water speed is one of the most complicated phenomena in corrosion problems. It is exceedingly difficult to separate out its specific effect from other associated effects. In the first place, it is now known that the speed of the water in a tube varies greatly across the transverse section of the tube. In the centre of a tube the velocity may approximate to twice the average speed calculated from the total volume of water passing. Near the walls, however, the speed may approximate to zero, or even assume a negative value, with the formation of eddies; it is the speed near the walls that is most important in corrosion matters. Generally speaking, increased speed means increased corrosion.

"If a tube has been in service for some time and acquired a rough surface due to scale accumulation, etc., the eddying effect may be expected to be more pronounced than in smooth tubes, and consequently a knowledge of the average speed of the water passing through the tube will give very little information as to what is happening at any specific position at the tube wall. Eddies tend to assist corrosion, and eddy centres are liable to be pit centres.

"Another important matter in this connection is foam formation.

"The stream of water entering a condenser usually contains admixed air, and at certain speeds and with certain waters (of which sea-water is one) foams are formed. Such foams are particularly liable to be formed where a local increase in speed occurs, such as is brought about by a partial throttling of a tube for instance.

"Foams consist of intimate mixtures of air and water, in which the individual spherical bubbles of air, such as occur in clear water, are no longer clearly visible and the mixture becomes opaque. The opacity is due to the extreme subdivision of the air and the consequent intimacy of mixture.

"Such a foam may be fairly stable, and only slowly separate into large air bubbles and water. It may exhibit selective absorptive properties, and be much more corrosive than a clear water stream, or one carrying along large separate bubbles of air. Thus the tendency of a water to form a foam is an important factor in its behaviour as regards corrosion.

"Comparatively pure waters, such as distilled-water and many samples of rain-water, have little or no tendency to form foams. The introduction into a water of a substance which lowers its surface tension, such as sodium chloride, increases its tendency to foam, hence sea-water readily foams.

"The permanency of a foam is greatly affected by the viscosity of the water, an increase of viscosity increasing the permanency of the foam. The permanency of a foam in tubes through which sea-water is passing is sometimes remarkable, and may result in what may be described as a 'foam clot' in certain positions in the tube. The formation and position depend partly on the water speed. Thus, in certain experiments with sea-water a 'foam clot' appeared at the top inlet ends of the tubes extending for about 5 inches into the tube. This happened with average water speeds of 5 to 6 feet per second; if the speed were dropped to 2 to 3 feet, the clot disappeared, and was replaced by a clear-water stream containing separate bubbles.

"If the sea-water used in these experiments were replaced, for instance, by London tap-water, no foam could be formed at any speed up to 6 feet per second; the amounts of bicarbonates and salts present in such waters are small as compared with the amounts present in sea-water and do not sufficiently lower the surface tension and increase the viscosity to produce a stable foam or froth. Condenser tube corrosion is almost unknown in such waters.

"The principal factor in producing foaming in sea-water is probably the sodium chloride; many other substances, however, behave in a similar way—for instance, many acids. Some typical substances which produce foams or froths are colloidal solutions and emulsoids, such as soap solutions, sewage discharges, and oil water mixtures, and these are effective when present in very dilute solution.

"Oils of many types form fairly persistent foams with air; creosote oil, for instance, such as may occur in a gas work's discharge, makes a stable elastic froth, as do many types of lubricating oil. Such oils, may, of course, be drawn into condensers in docks, rivers, and inland waterways, and form 'foam clots' in tubes at certain water speeds and initiate local action, and the action once started may continue even after the disappearance of the foam clot. This is one of the reasons why new tubes are liable to attack in builders' yards, certain reaches of the Clyde, the Manchester Ship Canal, and other places where oils and other foam-producing substances may be present in the water and may cause foaming in the condenser. (It may be pointed out that oils and some other substances which cause foaming are seldom reported in water analyses, and it is desirable that the analyst should be especially asked to look for these in cases of condenser tube corrosion.) Old tubes may have a covering of carbonate scale on their surfaces which can defy the action of foams or froths.

"In this connection it should be borne in mind that there is a critical speed, depending on the length and diameter of the tube, which should not be exceeded if turbulent motion (which may itself produce frothing) is to be avoided. Turbulent motion, besides incurring corrosion, throws extra strain on the pumps.

"There are, however, some other facts to be taken into consideration when discussing water speed. William Ramsay, as the result of his experience of tube corrosion in ships on the Mersey, has come to the conclusion that too slow a speed may also cause the local corrosion of tubes by an entirely different kind of action. Such corrosion takes place at the inlet end of tubes, and he considers that it is caused by the accumulation of CO_2 gas at the top inlet end of the tube (owing, of course, to the rise in temperature), just as the water enters the tube.

"(*l*) ENTRANCE INTO CERTAIN WATERWAYS, ESPECIALLY WITH NEW TUBES

"It seems clear that tubes are most sensitive to adverse conditions when newly placed in the condenser. After they have been some time in use they tend to become covered with a scale that may be, and sometimes is, very protective, in which case the life of a tube may be extended to fifteen or even twenty years.

"After local corrosion has once started at any given spot, however, little or no protective scale will be formed over that spot, and corrosion will continue even under conditions that would not have initiated it. Some of the reasons why certain water-ways and docks are specially corrosive to new tubes have already been discussed.

"(*n*) UNSUITABLE DESIGN OF WATER-END

"In two pass condensers in which the circulating water enters the bottom pass, trouble sometimes occurs with the ferrules and tube ends where the water enters the top pass. This happens most frequently with condensers in which the free space in the water-end is unduly restricted; occasionally it is no more than 6 inches. The trouble appears to be due to the extreme agitation and consequent foaming of the water when negotiating the abrupt turn.

"Somewhat similar effects also occur sometimes in the first pass of condensers.

"(*o*) FERRULE TROUBLES

"It sometimes happens that the ferrules are made of 60/40 brass or screw metal, and that the ferrules give trouble owing to corrosion. These alloys are more sensitive to variations in corrosive conditions than 70/30 brass, and where such troubles occur it is desirable to use ferrules of 70/29/1 alloy. Leaky packing is liable to cause corrosion; also substances caught in or on the ferrules, such as clinker, wood shavings, etc., as described under (*f*).

"(*p*) TOO HIGH A TEMPERATURE

"Sometimes the high temperature of the cooling water is a source of trouble, especially in the tropics; in general, an increase in temperature increases the danger from both the white and blue types of attack. Occasionally the high temperature is local and due to an auxiliary steam supply. In condensers working at too low a vacuum the temperature of the incoming water may, of course, be raised considerably. In general an increased temperature means increased corrosion.

"(*q*) THE PRESENCE OF IRON COMPOUNDS

" Iron oxides and hydroxides in certain physical states are slightly soluble in sea water, yielding what is practically a solution of ferric chloride, a very corrosive substance. If such substances stick to a new or nearly new tube (*i.e.*, one which has not become coated with carbonate scale) a local attack on the tube may take place. Heavy lumps of scale from water mains and water-ends may act in this way; the ordinary flocculent hydroxide is readily swept away in the water-stream.

"(*r*) SHORT-CIRCUITING OF CONTAMINATED COOLING WATER

" This is occasionally liable to occur in the case of works situated on estuaries and rivers. The intake and outlet mains for the circulating water are sometimes taken out into the river to approximately the same distance. The intake jack-well may be thoroughly protected from seepage, but not the outtake jack-well. The water in the latter may then become contaminated with factory products, etc., and pass to the outlet main and, at certain states of the tide, for instance, be sucked in at the inlet main.

" A number of factors which may set up corrosion and lead to the failure of a tube have now been considered. It will be noticed that the majority of these factors are outside the control of either the tube-maker or the tube-user.

" In considering the prevention, or at any rate the retardation, of corrosion, it will be clear from what has been said already that the actual perforation of a tube is only occasionally the result of one factor only, it is more usually the final net result of a number of different factors. The relative importance of these factors in producing the final result is unlikely to be the same in any two condensers, and, in consequence, a remedy which may be found useful in one case may be quite useless in another. Hence experiments carried out in one plant or ship are of strictly limited value unless all the factors in connection with that plant are known. Such knowledge is difficult, if not impossible to obtain. Even such an important factor as the water speed is not usually known, and as a result the interpretation of experiments in commercial condensers is frequently uncertain. A further difficulty arises from the fact that the most obvious methods of protection from a chemical point of view are frequently impracticable from an engineering standpoint. For instance, water treatment would suggest itself as a desirable remedy for many tube troubles, but as far as ship condensers are concerned, any form of either physical water treatment, such as filtration or ordinary chemical water treatment, is barred, owing to the enormous bulk of water that has to be passed through the condensers. Electrolytic treatment of the water may, however, be used, and is the real basis of the well-known electrolytic protection processes. Possible protection processes are given in the following table.

" The following discussion of methods of lessening corrosion must be regarded as representing a summary of present knowledge, and is necessarily incomplete.

“ Possible Methods of Lessening Corrosion

“ 1. Use of standard alloys, *i.e.*, 70/30 brass, 70/29/1 alloy, or arsenical copper, combined with

1. Water treatment.
   - (*a*) Physical, *e.g.* filtration (impracticable on a large scale).
   - (*b*) Chemical, *e.g.* softening, neutralisation.
   - (*c*) Electrolytic, *e.g.* Harris-Anderson, Cumberland and Gush systems.
2. Tube treatment.
   - (*d*) Tube cleaning
     - (1) By rodding out.
     - (2) By acids.
   - (*e*) Annealing at low temperatures in oxidising atmosphere.
   - (*f*) Protection by layers of insoluble salts.
   - (*g*) Protection by metallic layers, *e.g.* of lead, or by inert substances, *e.g.* varnishes, bakelite, etc.

“ 2. Use of other alloys, with or without methods described under 1.

“ Of the methods tabulated, 1 (*a*) is not usually practicable on the large scale, excepting in the case of make-up water for the supply of cooling ponds, and 1 (*b*) is frequently a matter for the Water Authority rather than for the engineer in charge of a plant; hence 1 (*c*) will be first discussed here.

“ 1 (*c*) ELECTROLYTIC PROTECTION

“ In electrolytic processes the tube to be protected is made a cathode, *i.e.*, a negative pole, by means of a current passed to it, through the circulating water, from an anode of zinc or steel. The current may be generated merely by means of a metallic couple, or by means of an external battery or motor generator.

“ Electrolytic protection is the most widely used method of attempted protection. Its simplest form consists in the use of zinc or steel protector slabs in the water-ends, electrically connected with the tube plate or condenser body, and these form an electric couple with the tube to be protected. The use of zinc can be very briefly dismissed: it is inferior to steel for the purpose from several points of view, in spite of the fact that it is higher in the electrochemical series; it is more expensive, liable to reversal of polarity, and liable to form harmful products of corrosion which may pass into the tubes; it is also liable to great losses by exfoliation.

“ The use of steel protector blocks deserves more consideration. As in the case of zinc, these blocks form a couple with the tubes.

“ The points to be observed in connection with the use of steel protector blocks are stated below, and unless due attention is paid to them, little or no protection may be obtained. These points are:—

“ 1. The symmetrical distribution of the blocks opposite and parallel to the tube plate. In multi-pass condensers blocks should be placed at each end of each section of the water-box.

"2. The use of as many blocks as can be placed in the water-box without seriously interfering with tube renewals and water circulation.

"3. Prevention of short-circuiting, *i.e.*, the faces of the blocks should be nearer to the tube plates than to any part of the water-end.

"4. Proper bonding of the blocks by screwing into the tube plate so as to ensure good electrical contact (it is convenient to omit tubes and screw the blocks into the holes they would have occupied); alternatively all the blocks may be insulated from the water-ends and connected by cables to the tube plate, but this is more difficult to carry out efficiently.

"5. Renewal of the blocks before they become almost worn away.

"6. Good metallic contact between the tubes and tube plate, secured by insertion of a soft metal ring during packing. If the tolerance allowed between the diameter of the holes in the tube plate and the outside diameter of the tubes be very small, metallic packing may not be necessary.

"The protection afforded by such blocks does not extend very far into the tubes, certainly not more than 18 inches, and frequently less. Where troubles due to corrosion and not to erosion occur at the ends of the tubes, protector blocks may be useful; in practice they frequently fail, owing to imperfect installation.

"As an improvement over steel blocks, alloy blocks consisting largely of aluminium have been used considerably, and appear to have given distinctly better results, no doubt owing to the greater current generated.

"It is logical to expect that still larger currents generated outside the condenser by a dynamo or secondary battery, and kept at a constant value, say 3 to 5 amps. per 1000 square feet of protected surface, would be more effective than the use of protector blocks. Well-known electrolytic methods of protection have been founded on this principle. Their installation, of course, is much more expensive than that of blocks, and it is necessary to emphasise the fact that their effectiveness, as in the case of protector blocks, is largely dependent upon attention to a number of details in installation and upkeep.

"The principle of the process as applied to sea water is as follows :—

"When an aqueous solution of sodium chloride, such as sea water, is electrolysed, sodium ions pass to the cathode and chlorine to the anode; water is also electrolysed, hydrogen passing to the cathode and hydroxyl ions to the anode. In these conditions, hydrogen is given off at the cathode and chlorine at the anode (owing to the high over-voltage of the oxygen). Owing to the removal of hydrogen ions from the cathode, the liquid surrounding it becomes alkaline, since there is an excess of hydroxyl ions. Consequently, the cathode is surrounded by a dilute solution of caustic soda, a solution that only very slowly attacks brass, at condenser temperatures.

"In addition to this, any calcium which exists in solution as bicarbonate is precipitated on to the cathode as a thin film of calcium carbonate. This film has some protective value.

" Points to which attention should be particularly directed when installing electrolytic protection are the proper insulation of the anode, and its location nearer to the tube plate than to any point of the water-end (to avoid short-circuiting); measures should also be taken to prevent reversal of polarity.

" The claim has been made from time to time that corrosion troubles, whether in boilers or condensers, will cease to exist in any plant in which electrolytic protection is properly installed. This, however, is not the case. Corrosion phenomena are too varied and complicated in character to be susceptible in all cases to the same remedy. It is a fact that experimental data obtained in the laboratory, as well as observations made on plants with the electrolytic protection properly installed and working under practical conditions, both land and marine, show that such a wide claim cannot be substantiated. It is true that under a variety of conditions good results have been obtained; in other cases, however, little or no protection has been afforded, and it is obvious that one of the chief difficulties in the way of the process is the proper distribution of the current over the whole of the tube surfaces to be protected; usually protection is most effective at the ends of the tubes. A possible cause of the failure of protection under certain conditions is the mixing of the cathode and anode reaction products, so that the cathode is no longer bathed in caustic soda solution.

" One of the principal problems met with in practice, when utilising electrolytic protection, is the proper insulation of the anodes from the rest of the condenser. If this insulation should break down, or be even partially impaired, the current will, of course, be short-circuited through the body of the condenser, and only a small portion will find its way to the tubes which are to be protected. It is by no means an easy thing in practice to maintain the complete insulation of these anodes for long periods, and some of the recorded failures of electrolytic protection are to be traced to this cause. There are several patents which deal with the best means of maintaining the insulation, and the differences between a number of the electrolytic processes now on the market are largely due to the different methods of insulating the anode. When using electrolytic protection weekly tests should be made to ascertain that each anode is working properly, and it is advisable to place the installation in the hands of firms experienced in the matter.

" From what has already been said it will be clear that electrolytic protection will be most effective at the ends of the tubes, since the steel anodes are necessarily situated in the water-ends, and most of the protecting current will pass to the tube plate and tube ends. Less and less current will pass to the tube further in the condenser, and a minimum will be reached at the centre of the length of the tube. The protection afforded will be proportional to the current, and will be least effective at the centre of long tubes. Thus the conditions most favourable to the process are short tubes in which the trouble is confined to the tube ends, and in which a comparatively low water speed is used. Very shallow water-ends are not favourable to the process, owing to the danger of short-circuiting.

"A quite different method of water treatment has been proposed by F. de Wurstemberger, and is the subject of an English patent. The method is based on the idea that local corrosion is due to alkalinity (which causes the precipitation of basic salts) and that if this can be prevented local action will also be arrested. In order to prevent alkalinity a very dilute solution of ferric chloride is used. This may be produced by electrolysing sea water between iron electrodes, and passing the anodic product only through the tubes to be protected. The cathodic product, caustic soda, is prevented from entering the condenser. It is not, however, essential to this method of protection that the ferric chloride solution should be produced in this particular way. The writer has no knowledge of this process on a practical scale. Some rough tests have shown, however, that if tubes of Admiralty alloy be kept immersed in warm sea water in which strips of iron are also immersed, but not electrically connected with the tubes, the accumulation of copper basic salt on the tubes is much lessened, and local action is largely arrested. The brass remains bright yellow in colour and is slowly attacked by general roughening and more particularly along score lines. This suggests that any great excess of ferric chloride should be avoided, and only just enough used to prevent the precipitation of copper basic salt. This can best be decided by trial and error; in any case the necessary concentration is very low, and less than 0·1 per cent. If this process be of value at all, the special difficulty of protecting the middle of long tubes should disappear.

"2 (*d*) TUBE CLEANING

"Attention may first be directed to a rather unpopular palliative for corrosion, namely, tube cleaning by rodding out with wire brushes, etc. In certain cases this would no doubt be useful if it could be carried out systematically. Unfortunately, it frequently happens that the process is inconvenient, and this may partly be due to the restricted space in which the condensers are sometimes placed. In any case it necessitates the 'laying off' of the condensers. In no case, however, should coke, clinker, weed, wood shavings, shells, etc., be allowed to remain in the tubes or against the ferrules, even if they are not completely choked. Sometimes these substances are held in contact with the ferrules as long as water is passing, and thus set up an attack on them.

"The alternative to cleaning by rodding out is to clean by the use of acids, possibly followed by rodding out. There is something to be said for this idea. For instance, it is shown that certain foreign deposits which set up local corrosion are fairly easily soluble in cold acid, whereas brass alloys are but slowly attacked. Why, therefore, should not these deposits be dissolved off and local action stopped?

"There is no doubt that local action at any given spot could be stopped in this way. Nor is there any serious difficulty in using the acid, since appliances are already on the market for getting rid of the scale from condensers which are worked with hard water.

"Now, although it is perfectly legitimate to use acids for the removal of calcium carbonate deposits when these become so thick as to impair seriously the transference of heat, yet there is an objection to their use in other cases. The hard carbonate waters are not seriously corrosive as a rule, and when the bare metal has been exposed by the acid there is little danger of it being locally attacked when the tube is again in use. Soon a scale will again form and protect the tube.

"In sea and estuarine waters, however, really thick deposits of calcium carbonate scale are rarely found, except at the ends of tubes; but tubes become covered with thin composite scales, consisting of calcium carbonate and sulphate, basic carbonates and chlorides of copper and zinc, and oxides and hydroxides of these metals. The proportions of the various constituents of the scale differ at different points along a single tube, and in different tubes. Some of the constituents also undergo changes with time, temperature, and seasonal variation in the circulating water (such as occur in estuarine conditions). In fact, the scale may become locally liable to set up corrosive action, or it may be locally protective.

"Sometimes the scale may be extremely protective though quite thin, say $\frac{1}{75}$ inch in thickness. In such cases it usually contains a considerable proportion of calcium sulphate, as well as carbonate. In such cases it must, apparently, have been formed slowly, since the amount of calcium sulphate in sea water is quite small (less than 0·1 per cent.).

"Such a scale may, exceptionally, be formed over the whole surface of a tube. A condition of its formation is that, in the case of a ship, the ship shall not encounter, during its early life, badly corrosive conditions. If it do so, local attack may be set up at certain spots, and the protective scale will not be formed over such spots; it may, however, be formed over the general surface of the tube.

"It is clear, therefore, that though the acid may remove the harmful deposits which cause local action, it will also disintegrate the protective scale which contains calcium and other carbonates. Subsequently to the acid treatment, therefore, a new tube surface will be exposed, and there is a renewed danger of local action beginning owing to the absence of scale.

"Every time the acid is used there will be an increased possibility of starting new pits. It is true that the progress of the old ones will have been checked, and it might be thought that corrosion would have been evened up, which is a very desirable thing. There remains the possibility, however, that corrosion might make a new and independent start at one or more of the old pits where the tube wall is already thinned, and this would be disastrous. Whether it did so or not would be purely a matter of chance.

"The usual objection raised to acid treatment is that the direct attack of the acid on the metal would be serious. Experiments have shown, however, that if cold acid be used in concentration not much more than sufficient to attack ordinary scales, this factor would not be a serious one, as the acid treatment is not prolonged.

"As far as the present author is aware, no data from practice as regards cold acid treatment for corroded tubes are available, and the matter is mentioned because it affords an opportunity of dealing with the important matter of scale formation.

"2 (*e*) OXIDISING ANNEALING AT A LOW TEMPERATURE

"In the opinion of the author there is now sufficient evidence in favour of the use of low temperature annealing, say three hours at 350° C. in an oxidising atmosphere, to justify its more extended use in practice for 70/30 brass, 70/29/1 tubes, and, perhaps, arsenical copper.

"That tubes so treated will fail under extremely bad conditions is quite true, but when conditions are not so bad, but still bad enough to cause an annoying loss of untreated tubes, then the process appears to be of use. It has the advantage of adding only a trifle to the cost of the tubes. Specifications might well contain a clause calling for a final annealing at 350° C. ± 25° in an oxidising atmosphere, the process *not* to be followed by pickling.

"2 (*f*) PROTECTION BY LAYERS OF INSOLUBLE SALTS

"Sometimes the carbonate scales on tubes are of great protective value, and an obvious way of preventing corrosion would seem to be to prepare artificially such scales on the tubes before they were put into use.

"Many attempts have been made on these lines, but with only partial success. One of the principal difficulties appears to be the time factor. To get a really strong resistant scale, the deposition on the tubes must apparently be carried out slowly—extended perhaps over several months—a procedure not practicable commercially. Scales of many different types have been prepared and tested, but unless they have been very slowly produced they behave in a rather curious way. They may give apparently excellent results for a time, but at last become locally porous, and then swell up to form blisters. These blisters finally break and an enhanced attack takes place at such areas, and the initial protection of the scale is thereby more than neutralised. Such local attack appears to be due to the formation of a 'concentration cell' and is similar to an action which causes local pitting when naturally formed scales fail.

"This branch of study, however, has not yet been sufficiently explored, and there is still hope that something of value may be found along these lines.

"2 (*g*) PROTECTION BY METALLIC LAYERS

"A process that seems more immediately practicable is that of lead-lining a tube. Tubes lined with lead alloys and with lead itself were used by the German fleet during the war, and as far as can be gathered, gave good results. In order to secure adequate protection of the tube it is necessary that the layer of lead should have a certain minimum thickness. Very thin layers, though apparently continuous to the naked eye and to microscopic observation, are liable in time to become slightly porous. In such cases water slowly penetrates to the metal beneath the lead, chemical change begins, and the lead lining is liable to come away in flakes. The technical production of linings sufficiently thick to resist this action is, however, possible, and tubes so lined can be produced commercially in this country, if a demand for them springs up. They should only be used with low water-speeds.

"So far it has been supposed that the tubes to be protected were either 70/30 or Admiralty alloy. The next point to consider is the possible use of alloys other than these.

"The principal factor to be taken into account in the choice of a tube for condensers is, of course, the nature of the water supply. A very rough classification of the character of industrial waters as regards condenser tube corrosion is given below; it is based on the cases of good and bad behaviour of tubes that have come before the author, and is necessarily incomplete:

"(1) Waters containing little or no chloride, but much calcium salt and of high temporary hardness; *e.g.*, London water.

"(2) Waters containing little or no chloride and low in calcium salt and of low temporary hardness, but high in dissolved CO_2; *e.g.*, Lake Vyrnwy water, certain Australian waters, etc.

"(3) Waters high in chloride, but comparatively low in dissolved CO_2, such as sea-water.

"(4) Waters with moderate chloride content, but liable to contain considerable amounts of dissolved CO_2 at certain times of the year; *e.g.*, certain estuarine waters, such as lower reaches of the Tyne.

"All these waters are normally neutral or slightly alkaline to methyl orange.

"(5) Waters acid to methyl orange, containing small amounts of free hydrochloric or sulphuric acid, *e.g.*, certain canal waters and certain docks. The acidity may be due to oxidation of SO_2 in the atmosphere, pyrites, etc., or to acid discharges. The acidity may be temporary only.

"Waters condensed in cooling towers do not fall into any such general classification, since their composition gradually changes owing to salt concentration.

"1. Waters of the first type are not usually corrosive to brass alloys, and condenser tubes generally stand up in them for many years; 70/30 brass or Admiralty alloy is all that is required.

"2. Waters of the second type are frequently 'treated' in this country to bring up the calcium carbonate content. If this is not done such waters may seriously attack brass tubes, especially if a trace of chloride is present. In such cases it is advisable to replace 70/30 brass or Admiralty alloy tubes by some alloy containing neither zinc nor lead.

"3 and 4. Waters of the third and fourth types, but particularly the fourth, are those which give the most frequent trouble, and for some cases it is very desirable that a better alloy than brass should be discovered. In the first instance Admiralty alloy should be used; if this fails a 2 per cent. lead-brass tube is worth trying for estuarine-waters; alternatively, a copper-tin or an 80/20 copper nickel tube in the hard drawn state; but it is here that a new type of tube is most wanted.

"5. Waters of the fifth type behave differently from all the others, in that the tubes usually fail by general thinning instead of by local pitting, etc. In such cases arsenical copper tubes are superior to brass or Admiralty alloy, and 80:20 copper nickel is still better; the water speed should be kept low.

"It may be said generally that comparatively few alloys other than brass alloys and arsenical copper have been submitted to thorough trials under practical conditions, and most of these have been copper alloys containing nickel.

"The use of nickel, within the limits allowed by cost, appears to be sound in all cases in which chloride waters are concerned. In such waters chlorides of the constituent metals are liable to be formed, and such chlorides may be highly destructive of the alloy, *i.e.*, the alloy contains within itself the seeds of its own destruction. Thus cupric and cuprous chlorides are actively harmful substances and corrode both copper and brass. Compared to these substances, however, nickel chloride is a harmless material. Thus it would seem to be the logical thing to replace as much as possible of the copper of an alloy by nickel. The zinc, too, may be wholly or partially replaced by nickel, giving an alloy of the German silver type.

"As far as the author is aware, the alloy highest in nickel that has yet been tried for condenser tube work is monel metal. Trials were carried out in America some years ago, and the results are described by Shaw Sparrow. The tubes were stated to contain 69 per cent. nickel, 28 per cent. copper, and 3 per cent. other metals (iron, etc.). Shaw Sparrow concluded that monel metal is not proof against corrosion in salt water, and showed photos of tubes badly corroded after one year and eight months in condenser service, and another after only eleven months after simple immersion in sea-water. These results are rather discouraging, and it is possible that the 3 per cent. 'other metals' had a good deal to do with the result; probably iron was one of these, and its bad effect on brass has already been noted.

"As regards resistance to acid waters monel metal has given good results.

"Another alloy comparatively high in nickel that has been given a fairly extensive trial is the 20 per cent. nickel alloy with copper. This alloy was put on the market in America under the name of Benedict metal. It has the unusual property of permitting working right down from the hollow-cast shell to the finished tube without intermediate annealing, and the resulting tube is stiff enough to be used of slightly thinner gauge than the usual 18 gauge.

"Under estuarine conditions these hard-drawn nickel-copper tubes have given good results in this country and in America; the United States Navy has given an extensive trial to them and favourable results have been reported.

"Such tubes probably have a future before them. They are by no means incorrodible in sea water, but do not appear to be so sensitive to variations in conditions as brass alloys. They are now being made in this country, and since they have a reasonable scrap value when worn out, are worth a trial where continual trouble is encountered with brass tubes. There is some reason for thinking that these tubes will not behave well where the water speeds are high, such as 8 feet per second and over.

"Tubes with lower percentages of nickel, such as 5 and 10 per cent., are also being produced, but for sea water and estuarine work it seems probable the higher proportion of nickel is better. For certain fresh-water conditions the lower percentages might be sufficient.

"Aluminium-copper tubes, containing amounts of aluminium up to 8 per cent., have been proposed and tried from time to time. Although tubes of this alloy cannot be relied upon in sea and estuarine waters, it may be of interest to refer briefly to their behaviour, which is characteristic of a large class of corrosion phenomena.

"If, say, an 8 per cent. alloy be tested by complete immersion vertically in sea water, it usually happens that very little attack takes place, and the alloy may be reported as incorrodible even at the end of many months or even years under test. If the alloy be submitted to a water-line test, *i.e.*, suspended half in and half out of sea water, a considerable attack can usually be seen to take place near the water-line. The actual attack is patchy, and does not extend all round the water-line. The usual explanation of such an attack is that it is due to the depolarising action of the air, but this can readily be shown to be an insufficient explanation. The action is really due to the local sticking of certain products of corrosion, and does not take place to a noticeable extent if such action be prevented; the chemical action of the air increases the rate of local formation of harmful products.

"Although the general attack on the surface of the tube is slow, yet in time certain products will form, become detached, and float up to the water-line, and these may start an attack. The attack will take some time to develop, since the accumulation of products is slow. When once started, the attack is very violent.

"If the alloy be tested horizontally in the form of a tube, there is always the possibility of corrosion products sticking to the bottom of the tube, and if this occur before a protective scale is formed on the tube, very rapid failure of the tube may result considerably more rapid than in the case of 70/30 brass.

"In practice in condensers it has been found that tubes of this alloy may give either quite good or very bad results. Sometimes they give good results for a time, and then fail suddenly in large numbers. They are, in practice, unreliable, the quality most to be avoided in condenser tubes.

"It has been found possible in recent years to draw copper–tin alloys into tubes suitable for condenser work. Tests have been made on 5 per cent. phosphor bronze tubes and on 9 per cent. tin-bronze tubes. The former have not behaved well in sea-water, and the latter do not appear to offer any considerable advantage over Admiralty alloy. In waters which require an alloy that does not contain zinc, these tubes are worth a trial.

"Little is known at present as to the behaviour of triple alloys other than tin and lead brasses. Certain alloys of the copper–nickel-zinc or German silver type have been tried, but though they resist general attack pretty well, they are somewhat liable to rapid local attack. Triple alloys of copper–nickel–aluminium appear to be more hopeful, and are now being tested; triple alloys of copper, nickel and manganese are also under test.

"It is probable that a large number of triple copper alloys would be suitable for condenser tubes mechanically, but comparatively few as regards corrosion. A considerable field must therefore be explored to pick these out, and this work is now being carried out.

"*Memoranda*

"1. Under all ordinary circumstances use tubes and ferrules of Admiralty alloy (70/29/1). For exceptions from this rule see body of pamphlet (page 127 *et seq.*)

"2. Give preference to tubes in which the iron is guaranteed to be less than 0·1 per cent.

"3. A clause in specifications calling for an oxidising annealing for three hours at 350° C. ± 25° C. is worth a trial. Such tubes must not be subsequently pickled.

"4. When local corrosion has once started in a tube it is practically impossible to stop it, even by electrolytic protection, and tubes are most sensitive to bad conditions when new. Consequently, never allow new tubes to become wholly or partially choked, but clean out as frequently as possible; later in the life of the tubes this is not so necessary.

"5. Steel protector blocks, if used at all, should be put into condensers at the same time as new tubes.

"6. When using protector blocks or any other form of electrolytic protection, always use soft metal rings when packing tubes.

"7. Electrolytic protection by motor generator or battery is worth a trial if tube losses are heavy. It should be applied to new tubes, and maintained continuously, and not intermittently. The details of the installation require careful consideration, and is a matter for experts. Careful watch must be kept for reversal of polarity.

"8. Leaky packing is a possible source of corrosion of tube and ferrule.

"9. Auxiliary supplies of steam should be taken into condensers with the main supply at the top, and not separately at the sides.

"10. An alteration in water speed may have striking results on the number of tube losses. No general rule can be given in this matter, but trials are worth making when corrosion troubles are serious. If the vacuum in the condenser is low, try raising the speed first, but not above 6 feet per second; otherwise try lowering it first. With very high water speeds, such as 10 feet per second and above, greatly increased trouble is to be expected with arsenical copper tubes, and probably with some other tubes also.

"11. Foaming is a serious cause of increased corrosion, so any possible measures should be taken to prevent it, *e.g.*, stop any air leaks in pipe line or at pump. Water containing oil is liable to be specially dangerous.

"12. Whenever possible, avoid exposing *new* tubes to attack by waters liable to be foul, such as the Manchester Ship Canal, the Tyne, the upper reaches of the Clyde."

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PART III

THE PREVENTION OF CORROSION

CHAPTER X

THE CONTROL OF IMPURITIES AND MANUFACTURE—CARE IN DESIGN, ETC.

IT should be stated at the outset that the heading accorded to this section is misleading and open to criticism. "The Prevention of Corrosion" is a popular term, and has been chosen for this reason, but the subjects about to be discussed would be more accurately represented by the title "The Protection against Corrosion."

Most of the protective measures which will be dealt with are but palliatives in the sense that they do not afford permanent protection to the metal to which they are applied and none of them overcome or destroy the inherent tendency of ferrous material to corrode. Many of them protect the iron or steel at their own expense and for a period which corresponds more or less closely with their own period of perfection, and they must be frequently renewed if the protection of the metal is to continue. There are but two aims which are common to all protective or preventive measures, either (1) to exclude corrosive influences from the metal surfaces or, where this is impracticable, to (2) remove the corrosive influences from the vicinity of the metal.

The practice of applying protective coatings, whilst of undoubted value, may be likened to locking up a house with a thief already inside it. Keep the house locked and all may be well, but the thief is an adept in effecting his exit at the weakest point. This is precisely what must be anticipated with protective coatings of all kinds, so long as they are maintained sufficiently strong to prevent the thief or corrosive influence from obtaining its freedom, the metal will be protected; permit one weak spot and the goods will be stolen or corroded. To obtain the ideal, that is, material which is non-corrodible, yet as satisfactory from a mechanical point of view, is not at present attainable, but the time may come when we shall have acquired the knowledge necessary to produce such metal. Advances have already been made in this direction. If, and when, this ideal is attained an enormous amount of time, labour, and material, which at present is expended in postponing the corrosion of iron and steel, will be saved.

Reverting to the title "The Prevention of Corrosion," the methods available fall readily into the following classes—

1. Prevention by means of Oxide and Non-Metallic Coatings.
2. Prevention by means of Metallic Coatings.
3. Prevention by means of Paints and like materials.
4. Prevention by processes of Water Purification.
5. Prevention by means of Electrolytic methods.

The first three classes function by excluding corrosive influences or preventing their access to the metal surface, and they are widely employed on both structural and other classes of material. Methods 4 and 5 operate by removing corrosive influences, or in the last case by overcoming them, and are principally confined to the alleviation of corrosion troubles which arise in the various units of steam-raising plants, and which constitute one of the most important of corrosion problems.

There might also be included various precautions, which in themselves appear somewhat trivial and insignificant, and which may, in fact, be actually of but minor importance, for there is little doubt that, of the forces working for corrosion, those external to the metal are very much more powerful than those inherent in the metal and are more rapid in action, and that to seek to correct these latter is, more often than not, incompatible with mechanical and other requirements. Nevertheless, when these precautions are disregarded, they add to the total of the corrosive forces which attack the metal. If they are appreciated and paid the attention they merit, the useful period of service of the metal may often be increased by an acceptable percentage. Many of these points will present themselves conveniently in other portions of the text, but some of the more significant will now be briefly considered.

The first precaution is one which gets well down to the root of the problem, but it is, unfortunately, one which is not readily put into practice, namely, care in the manufacture of the material. It is generally accepted that the careful control of impurities and the homogeneous and uniform distribution of essential constituents, coupled with a suitable and carefully controlled heat-treatment, will go far towards improving the resistance to corrosion of iron or of steel, simply by ensuring a uniform product. The craze for tonnage is probably responsible to a large extent for the reputed poor resistivity of many modern commercial irons and steels. High-speed production and methods of working tend to result in a metal which is porous, heterogeneous, and contains occluded gases and various other impurities and in which are developed internal stresses and strains and segregations, all of which are detrimental from the point of view of resistivity to corrosion. The remedy lies, of course, in more carefully controlled production and subsequent working and in annealing wherever possible. For immediate economic reasons these points are often disregarded (except, of course, where such treatment is essential to desired mechanical properties), since most of the metal produced receives some form of protective coating when put into service, and it must be admitted that in many cases this disregard is justified, not only for immediate, but also for general economic reasons.

There is a wide range of material, however, which, by reason of the nature of its service, must remain unprotected. The mechanical conditions, for instance, may be so severe that no protective coating would survive even a few hours, and other alternatives which may be available in the case of boiler tubes and economisers, etc., are equally impracticable. The preservation of this particular class of material would seem to be attainable only through an increased resistivity resulting from chemical purity and uniformity. This is almost entirely in the hands of the manufacturer.

It is of little value to contrast unfavourably our modern products with those of olden days. Obviously there is no comparison between the conditions under which the older material served and those to which most of the present-day material is subjected in the large industrial areas. The prevailing industrial atmospheric and general conditions are such that the best of the old materials would require artificial protection of some kind to ensure their permanence, that is assuming, of course, that they would fulfill the mechanical requirements. It would not seem worth while, therefore, to revert to the older and more tedious methods of production in order to obtain material which in itself is but a few degrees more resistant and which will still require the same artificial protection which is given to our modern metals. In many instances the mechanical conditions to which metals are subjected whilst in service may often be directly responsible for lowering their resistivity. Metal may be strained beyond its elastic limit, for example, and this, as we know, is equivalent to facilitating electrolytic action.

The design of structural material is another point to which attention might be drawn. In this class of material there occur opportunities for putting into practice certain precautions which may have beneficial effects on the life of the structure. Care in design can be directed, not only to reduce the risks or severity of corrosion, but also to facilitate the employment of protective measures. Wherever possible, the avoidance of lodging places for moisture and rain should be an objective. In large structures this is not easy and is frequently impossible to arrange for, yet it may often happen that severe local corrosion, due directly to such lodgments, occurs in places where it dangerously weakens the whole structure, whilst the bulk of the material remains almost perfect in condition. It may readily be imagined, for instance, that continued corrosion at the feet of tie-rods and stay-bolts, etc., is a lively source of danger, and it is usually found that these places are the ones most difficult of access to workmen when the structure is being repainted. The corrosion products cannot be efficiently removed by the scrapers, and the new paint is then applied to surfaces to which are adhering flakes of rust and which are also often damp. The best of paint applied under such conditions is of little use, corrosion proceeds underneath it and the accumulation of rust pushes away and detaches it in a short time and then the local conditions are just as bad as before the paint was applied.

The design should be such as to permit of ready accessibility to all parts for inspection, cleaning, and repainting purposes. Unnecessary and ornamental elaborations on large structures are best omitted in order to facilitate cleaning and repainting, and on these occasions the cleaning should be thorough both with regard to old paint and to the complete removal of all patches of rust. This latter point is one which is often imperfectly carried out, if not altogether neglected.

Contact between dissimilar metals, and even between different types of the same metal, should be avoided wherever possible. The reasonableness of this observation is well illustrated by the measure of protection which may be afforded to iron by those methods which involve the properly controlled contact between it and a dissimilar metal. The dissimilar metal employed in these processes is zinc, which, having regard also to supplies and cheapness, is the most electro-positive metal to iron. If appreciable protection can be thus obtained by a controlled galvanic stimulus, it is clear that the same stimulus, if uncontrolled in direction, can effect a considerable acceleration in the rate of the destruction of the iron. Much of the non-ferrous material used in connection with iron and steel is electro-negative to these metals and may therefore directly assist in their corrosion.

No two varieties of ferrous material are electrically neutral to one another, and if in contact the corrosion of the more electro-positive metal will be accelerated by the presence of the less electro-positive variety.

Where mechanical requirements will permit regard should be given to these considerations. From a purely corrosive point of view, it is not the best practice, for instance, to build a condenser of which the shell is cast iron, the tubes of 70/30 brass, and the tube plates of some other copper alloy, or to rivet boiler plates with any kind of rivets other than those made from the same material as the plates.

In many cases it is possible to determine precisely what are the most severe or virulent corrosive influences, and material should be chosen for service under these conditions which has been proved by experience to be the most capable of resisting them. Somewhat similar considerations apply also in the choice of protective coatings, thus a galvanised or other form of zinc-coated surface would not be chosen for service where the conditions were known to be acid.

CHAPTER XI

OXIDE AND NON-METALLIC PROTECTIVE COATINGS

The Barff Process.—The protective properties of the black or magnetic oxide of iron towards the parent metal have been appreciated for many years. Lavoisier, the French chemist, drew attention to its permanent character, and, later, Faraday noted the protection which this oxide afforded in the case of superheater tubes in which it was formed. As a result of similar observations, Professor Barff investigated the mode of the production of magnetic oxide with the express intention of utilising, to the best advantage, its protective qualities, and about the year 1876 he took out a patent for the process he had evolved. This process consisted in passing steam, superheated to 540° C., over the iron, which was contained in a closed furnace or retort, heated to about 1000° C.

The Bower-Barff Process.—It has long been known that sufficiently high temperatures will "blue" iron, even in the absence of steam, direct, or molecular, or dry oxidation being responsible. The next step in developing this form of protection was taken by Bower, who endeavoured to dispense entirely with steam. He was unsuccessful, however, in obtaining the desired result, that is, the magnetic oxide coat, since the duration of the treatment necessary to produce a reasonably stout coating also resulted in the formation of the red or ferric oxide. To overcome this difficulty, he made use of producer gas to reduce the ferric oxide, and his process then involved forty minutes' air treatment followed by twenty minutes' producer gas treatment, this sequence being repeated until the desired thickness of coating was produced. Later, Bower acquired the Barff patent, and there resulted the Bower-Barff process in which the metal parts are heated to about 900° C. in a closed retort into which superheated steam is conducted for twenty minutes. A mixture of the red and black oxides of iron is produced. The superheated steam is then cut off and replaced by a stream of producer gas, which reduces the red oxide to the black or magnetic variety. Repetitions of the process are carried out until the oxide coating is sufficiently thick, and finally an additional protection is given to the treated parts by the application of paraffin, which also gives them a good black colour. The production of the red oxide in this process may appear contradictory to previous statements which have been made, but the excessively high temperatures employed, round about 1000° C., will go far towards explaining this. The catalytic dissociation of the steam by the iron at these temperatures probably results in the production of such a large proportion of oxygen that the gas is able to further oxidise the first formed magnetic oxide to ferric oxide.

These processes give to the metals to which they are applied a very good protection, especially against acid fumes and, it is generally claimed, against sea water. Their use, however, is restricted for many reasons. There is, in the first place, of course, a limit to the size of the material which can be accommodated in the retorts or furnaces. Secondly, the temperatures employed prevent their application to metal whose mechanical properties are of importance, and which would be thereby adversely affected. Tempered materials, for instance, cannot be treated in this way. Further, the parts are slightly enlarged during the process, and thus it cannot be used on material in which close dimensional limits have to be maintained. Metal protected by this means cannot afterwards be bent or machined or worked in any way, because the magnetic oxide skin is too brittle to withstand deformation, and would crack and "flake" off. The process is a costly one and is not very extensively employed.

Magnetic oxide is strongly electro-negative to iron, and it is desirable to point out at this stage that the protections afforded to iron by oxide coatings, and in fact by all protective skins of a similar or metallic character, have a common drawback or disadvantage. They all cease to fulfil their proper function as soon as their continuity is broken, independently of whether the coating be electro-positive or electro-negative to the iron. In the case of the electro-negative magnetic oxide, so long as the coating remains perfectly continuous, efficient protection is afforded by it, but if, through any cause, its perfection is spoilt and the iron beneath it exposed, it will then commence to function as an accelerator of the corrosion of the electro-positive iron, and the corrosion of the latter will be rapid and deep. For this reason some authorities state that electro-negative coatings are not generally to be recommended. In the second case, where the coating is electro-positive to the iron, protection is again dependent upon the continued perfection of the coating. If the underlying metal becomes exposed in some parts, either by accident or through the deterioration of the coating, then, although it is true that the electro-positive character of the coating will prevent it from itself accelerating the corrosion of the exposed iron, and will rather tend to retard this, yet the electro-negative iron will accelerate the corrosion of the protective coating and hasten its solution or removal. This observation is of special significance, since the most widely used material in the production of electro-positive coatings is zinc, and this metal is very susceptible to, and rapidly corroded by, the same influences which attack iron. In many cases its corrosion is even more rapid than that of iron or steel. Iron, to which has been applied by any of the processes available an imperfect or porous coating of zinc, hastens its own corrosion, therefore, by accelerating the solution or removal of its protecting layer of zinc. These considerations will explain the remark made in the preceding chapter, namely, that "many of them protect the iron or steel . . . for a period which corresponds more or less closely with their own period of perfection."

It is not intended to belittle the use of such types of protection, but it appears very desirable to indicate their limitations. Thus, although the Bower-Barff process cannot be successfully or advisedly applied to many varieties of material, yet it has considerable value, for instance, in treating pipes and other rigid structural material and for railings, grillings, and metallic ornamental work, and also for builders' hardware and certain domestic articles. The general appreciation which this type of protection has received is evidenced in the numerous modifications and improvements in the process of its application which have been advanced from time to time.

The Wells' Process.—The original Barff and Bower-Barff processes were introduced in this country. The first modification of them was put into operation by Wells in America and consisted merely in using steam and producer gas or carbon monoxide together, and not in succession. The process differs, therefore, only in the fact that it is a single stage one instead of a double stage one, the results are identical with those obtained by the Bower-Barff process, and any improvement would appear to be confined mainly to an economy of time.

Gesner's Process.—Following on the Wells' process came the Gesner process, and this can more justly claim to be an advance or departure from the Bower-Barff method, since the coating produced is considered to be a compound of iron, carbon, and hydrogen, and has a lesser tendency to scale off than the magnetic oxide, that is, it is less brittle and more elastic. The hydrogen content of the coating is shown by analysis to be not lower than 2 per cent. The material which is to receive protection is placed in a retort and heated to 600° C., this temperature being maintained for about half an hour. Low-pressure steam, which has been partially dissociated into hydrogen and oxygen by being passed through a red-hot pipe in the bottom of the apparatus, is then allowed to act at intervals on the iron for a further half hour, after which there is introduced into the retort a small quantity of a hydrocarbon oil. This is given fifteen minutes in which to act and carbonate the surface of the metal. The process is said to be less expensive than the Bower-Barff process, and has also the advantage that there is less danger of warping or burning the material owing to the lower degree of heat employed. It is also claimed that little or no increase in size of the parts treated is occasioned.

The Dewees-Wood Process.—This process is almost identical with the Gesner process, and consists in exposing the metal to the combined action of superheated steam and hydrocarbon vapours in a suitably designed apparatus. It bears a similar relationship to the Gesner process as does the Wells' process to the Bower-Barff process.

The Bradley and Bontempi Processes.—Other processes which are similar in essentials are those of Bradley and Bontempi. The first of these, protected in 1908, consists in heating the articles in a furnace to a dull red heat and passing hydrogen gas over them followed by small amounts of paraffin to improve the colour. The hydrogen presumably serves to reduce the red oxide formed by high-temperature atmospheric oxidation. The metal, which is first thoroughly cleaned by pickling or sand-blasting, is allowed to remain in the furnace until a sufficiently thick coating has formed. When cold, the articles are treated with paraffin or linseed oil. The second process, the Bontempi, makes use of steam and a heavy hydrocarbon oil, tar or pitch, or the fumes from burning zinc. The use of the latter would tend to place this process in another category, as will be seen later.

The Ruffington Process.—The employment of excessively high temperatures and the attendant disadvantages thereby conferred on such processes have been overcome to some extent by procedures of a type which is well illustrated by that of Ruffington, in which the necessary temperatures are relatively moderate. A mixture of potassium nitrate and manganese dioxide is fused in an iron pot and the metal to be treated is immersed in the molten mixture for a few seconds and then suspended in the fumes over the pot. They are finally cooled in boiling water. The temperature need not exceed 350° C., and the metal is only subjected to it for a short period.

In a similar manner, attempts have been made to produce sulphide coatings and phosphide coatings on iron by exposing the metal to the fumes from suitable materials. Such methods have not, however, come into general use, and are not, as a rule, successful.

Electrolytic Processes.—Recent years have witnessed the investigation and development of electrolytic methods for producing black or magnetic oxide coatings and also for inducing a permanently passive condition of the metals treated.

If a piece of iron is made the anode during the electrolysis of water, oxygen is liberated on its surface, and if hydrogen is also present occluded in the metal, there will result a film of the black magnetic oxide. Ordinarily, however, such a film would be exceedingly tenuous, because of the small amount of hydrogen which is normally occluded in the metal, and in order to ensure a sufficiency of this gas, the iron is first made the cathode during the preliminary stage of the electrolysis, when it absorbs or occludes the hydrogen liberated on its surface under these conditions. The use of alkaline solutions in this connection is more common. One process makes the iron the anode in a hot caustic soda solution, and it would seem that by varying the amperage and voltage, the metal can be rendered passive or be coated with magnetic oxide. The passive condition so produced is said to be relatively persistent, but considerable advances will have to be made before it is sufficiently permanent to be of practical value.

A very recent patent covering the electrolytic production of an oxide protective coating is that of Rondelli and Sestini, B.P. 161127, 1920. The material, which may be of copper or copper alloys, as well as of iron and steel, is immersed in a hot solution of a fixed alkali, which contains also a copper compound such as the oxide or sulphate, and connected electrically in such a manner that it acts as the anode. Electrolysis is carried out at a temperature of 120° to 130° C. and with current densities up to 30 amperes per square decimetre. By varying the several factors, such as time and current density, etc., different coloured coatings are produced, ranging from light green to black. The black coating can be polished and resists corrosion. In the case of copper and copper alloys, a black copper oxide is obtained which acts in a similar manner to the oxide of iron in protecting the underlying metal.

There does not appear to be much recorded experience with this type of coating or any information as to its durability compared with oxide coatings produced by other means. If it is assumed to be equally good, however, then the only serious objection which might be raised against the electrolytic process is the probable embrittling of the ferrous material by the occlusion of hydrogen, of which a substantial residue may be left at the completion of the treatment.

Heat-Bluing.—The pleasing blue colour exhibited by thin magnetic oxide coatings is produced in a variety of ways and principally with a view to its decorative effect, for such coatings are comparatively poorly resistant to corrosion. Small articles, such as clock- and watch-hands, watch-cases, buckles, small arms, etc., are often heat-blued to give them a finish. The commoner methods are: dipping into fused potassium nitrate, heating in charcoal, and simply heating in air or tumbling in gas-heated sheet-iron barrels. They all aim at perfection of colour and appearance rather than the provision of adequate protection.

In concluding this section dealing with protective coatings which are essentially magnetic oxide skins, it may be stated that any of the processes which yield a heavy, compact, and closely adherent and perfectly continuous covering, may be relied upon to afford a reasonably good protection in most cases where the material is not likely to suffer mechanical damage. The limitations of magnetic oxide coatings should not be lost sight of, however, particularly in view of their electro-negative character. These coatings are never absolutely rust-proof, and even if they remain undamaged by mechanical agencies, they usually develop rust spots in periods which are longer or shorter according to the severity of the conditions of service and, of course, to the original good quality of the coating. Their tenacity to the metal on which they are formed is a factor which considerably enhances their value, for even when localised breakdowns occur, the corrosion of the underlying metal, although accelerated in these localities, spreads with difficulty, and is not readily able to destroy or push away the adjacent coating, as is frequently the case with other protective coatings. In many cases, however, it may be easily imagined that this restricting effect is more to be guarded against than is the more uniform corrosion, since it results in very deep pitting.

The Coslett Process. Passing attention has already been drawn to the fact that attempts have been made to produce sulphide and phosphide protective coatings on iron, and a rough indication of the procedures followed has been pointed out. The first, and apparently the only successful, technical process for obtaining a phosphatic coating was that introduced by Coslett, and it is one of comparatively recent origin, being developed in 1907.

The processes so far dealt with, and which are similar in principle and result, give fairly good protective skins of magnetic oxide and in some cases, also, a very pleasing and durable finish. They are, however, uneconomical both in time and material (expenditure of heat) and often involve several operations. Again, where high temperatures or combinations of fused salts are employed, the personal factor, as affected by the skill and experience of the charge-hands or foremen, is of considerable significance. The coslettising process eliminates many of these undesirable features by its simplicity and the readiness with which it lends itself to standardisation. Very low temperatures are necessary, and hence there is no risk of affecting the mechanical properties of the metal treated. Very fine springs, for instance, may be coslettised without their elasticity being impaired, and the treatment of magnetised material is without any effect on the magnetisation.

The material to be treated is first suitably cleaned by pickling or sand-blasting and then immersed in a hot solution for periods which are varied according to the nature of the articles and the thickness of the coating desired. The deposition of the coating is analogous to the deposition of copper on to iron when the latter is placed into a solution of copper sulphate. It is the result of the action of an acid solution of iron phosphates on iron. A solution of phosphoric acid will dissolve ferrous phosphate in quantities which are in direct proportion to the concentration of the free acid, and on introducing a piece of iron into such a solution, the free acid reacts with it and produces more ferrous phosphate, as a result of which the latter is precipitated from solution on to the iron at the points of solution of the metal. The solution is saturated with iron phosphate to begin with, and this condition facilitates the deposition of the coating, which is accompanied by the evolution of hydrogen and continues until no more of the base metal remains exposed. The iron is then completely covered with a continuous skin of basic iron phosphate or ferroso-ferric phosphate.

The solution is prepared by mixing iron filings and concentrated phosphoric acid into a paste and then adding this to a weak boiling solution of phosphoric acid. Zinc filings are sometimes used together with or even instead of iron, and in this latter case the phosphatic coating may be looked upon as the result of an interchange of metallic bases.

The coating is produced mainly at the expense of the surface layers of the material which is being coslettised. These go into solution and are replaced by an equivalent quantity of the metallic phosphate. The dimensions of the articles are consequently increased but very slightly, if at all, and the process is adaptable to the treatment of fine and delicate parts. It has been successfully employed in giving protection to very delicate surgical instruments, which are so fine that the slightest traces of corrosion would ruin them. It is a favourite process with type-writer manufacturers, and is claimed to be extremely efficient in protecting the multiplicity of small parts, which enter into the construction of these machines, under especially bad conditions. The coslett coating has also to recommend it the fact that it is particularly tenacious to the metal on which it is deposited. When properly applied, the coslettised material may be excessively and destructively deformed without the occurrence of any peeling or flaking away of the phosphate skin.

The colour of the coatings is a uniform dark grey, varying slightly in tone with the cleaning process to which the materials have been previously subjected. It is usual to dip the coated parts into paraffin or some other oil in order to change this colour to a deep black. In addition to the materials already mentioned, coslettising is well adapted for the treatment of tools, small mechanical parts, motor parts and ordnance, and also for marine use, since it has been found that marine growths will not attach themselves to phosphatic coatings. Further, this method of applying protection possesses the very desirable feature of filling up or closing small pores or blow-holes in castings and of doing this so efficiently that the articles will stand considerable pressure over such hidden defects.

The phosphatic coating itself is very resistant to normal, saline and acid atmospheres and to sea water. It is not, however, so well fitted to withstand wear or abrasion as are certain other forms of protection, and is generally less resistant to acids than the magnetic oxide coatings. It is much cheaper, however, and more simple to produce, and the process gives more uniform, and hence more reliable, results.

The Parker Process.—In common with all technical processes, the coslett process is not fool-proof. In other words, carelessness and inefficient control may result in the development of defects, such, for instance, as the adherence to or inclusion in the coatings of other materials from the bath, necessitating subsequent washing or other treatment of the articles. A patented modification of the coslettising process is that known as the "Parkerising" process. It differs from its forerunner by adding to the original coslett solution a quantity of manganese dioxide, with a view to partially oxidising the ferrous phosphate. The solution is boiled and stirred until the proportion of ferrous phosphate to ferric phosphate is as 3 is to 1. The resultant coatings are, however, comparable in all respects to those produced by the coslettising solution; a certain quantity of the manganese may be deposited conjointly with the iron phosphates as manganese phosphate, but as this is also rust-resistant and is not detrimental to the protecting quality of the coating, it does not introduce any objectionable features.

The principal function of the manganese dioxide is to oxidise the ferrous phosphate, and it appears to effect this catalytically. It may therefore be replaced by air or oxygen, but such a procedure would seem likely to result in complications in cases where the articles are of such a form that they can entrap the air which is blown into the solution. The composition and uniformity of the coating and its colour would probably be affected.

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CHAPTER XII

METALLIC PROTECTIVE COATINGS

PROTECTIVE coatings of a metallic character are clearly divisible into two classes according to their electrical behaviour in relation to the metal to which they are applied :—

(1) Electro-positive coatings.
(2) Electro-negative coatings.

It is often contended that the application of the second class involves greater risks of the corrosion of the protected metal than does that of the first class, since, once their continuity is broken, the exposed metal beneath, being then the electro-positive component of a metallic couple, will corrode preferentially. This cannot be disputed, but it would seem desirable to point out, however, that probably the only difference in this respect between the two classes is a slight variation in the time factor. If the continuity of an electro-positive coating is broken and the protected metal exposed, the same influences which, in the above case, results in the preferential solution of the protected metal will, in the case of an electro-positive coating, result in the preferential corrosion and consequent removal of the protection, and in this way more completely expose the underlying metal to attack. Moreover, since iron stands fairly high in the electro-chemical series of the metals and has, therefore, a comparatively high solution pressure, it follows that any metal which is electro-positive to iron must have a higher solution pressure. Hence, the removal of a protective coating of such a metal, by influences which become operative when its continuity is broken, will be rapid.

Of the metals electro-positive to iron, zinc is the one which commands most attention, both by reason of its cheapness, easy application, and the quantities available. It is, in fact, with but one exception, namely, aluminium, the only metal which finds any extended commercial application as an electro-positive protective coating, and it is very extensively used. Iron, protected by a properly applied coating of zinc—that is, one which is non-porous and continuous or unbroken—will withstand normal atmospheric conditions well, and so long as the coating remains perfect in the sense indicated above, any corrosion will be confined to the zinc. Even should its continuity be destroyed and the iron exposed, the tendency will still be for the more electro-positive zinc to corrode, rather than the iron, and it is in this manner that the protective influence of a zinc coating is exerted, namely, at the expense of its own destruction. Once the perfection of a zinc coating is destroyed, however, the protection afforded by it soon ceases to be of any value.

Zinc corrodes under the same influences as does iron and in much the same way, and as the electro-positive member of a galvanic couple, which has also a relatively high solution pressure, its solution and removal are very rapid even though, in some cases, the products of its corrosion may exert a retarding influence on the process. This is the principal objection to the use of zinc, and is also coupled with the fact that zinc coatings are frequently porous, or non-continuous to commence with, and that they are easily damaged mechanically. In the majority of cases, also, the purity of the zinc applied is by no means exceptional and impurities have the same effect on the rate of the corrosion of zinc as they have in the case of iron and for the same reasons.

Electro-negative metallic coatings are typified by those of tin, lead, and copper. These metals have low solution pressures, and on exposure to the usual atmospheric influences are attacked very slowly and the products of attack are protective, rather than otherwise, against further corrosion. Given perfect continuity in each case, therefore, an electro-negative coating of tin or copper should be more permanent than an electro-positive one of zinc, and a general condemnation of electro-negative coatings is scarcely justified, particularly when it is remembered that, with but a very occasional exception, no metallic coating will give protection for a reasonable period except under tranquil conditions, such as the exposure of structural material or that which is not subjected to abrasive or erosive influences whilst in service.

It is not the intention to discuss unfavourably the use of metallic coatings, nor to imply that those of electro-negative metals are superior to those of electro-positive metals, or *vice versa*. Both types, if properly applied to material the nature of whose service is not of a kind to inflict mechanical damage on the coatings, will give useful protection. Yet it cannot be questioned that both classes have the same drawback in that they cease to fulfil their proper function as soon as their continuity is broken. Since, however, their sphere of useful service has its limits, as indicated above, and the more commonly used electro-negative metallic coatings corrode less rapidly than do the electro-positive metallic coatings, yielding also products which normally still further reduce their rates of corrosion, it would appear that their more general use has been a neglected study and that the universal use of electro-positive metals in applying protection has become something of a fetish, akin to the practice of introducing zinc plates into boilers, amongst consumers. No doubt the ease, cheapness and variety of processes by which the principal electro-positive metal, zinc, can be applied is to a large extent responsible for this preference. After all, assuming that the protective coating is initially perfect, its chief desideratum is its own permanence, and those metals lower in the electro-chemical series are much more resistant to normal corrosive conditions than are those which are electro-positive to iron.

Protective Coatings of Zinc. Zinc may be applied to iron by four methods :—

(1) The Hot-dip process.
(2) The Sherardising process.
(3) The Electrolytic process. Zinc plating.
(4) The Spraying process.

The first three are widely used and each has its own advantages to recommend its adoption in certain cases. For instance, the soldering action of the hot-dip process is useful when the protected material is required to be water-tight, it is quick and generally ensures a thick, but often very impure and uneven, coating. The Sherardising process gives a very uniformly distributed coating, and is therefore preferable where machined material, etc., is concerned. The coating is also alloyed with the underlying metal, and thus there is no likelihood of its peeling away as may occur in coatings produced electrolytically. Zinc plating has the advantage that it can be carried out in the cold and gives a coating of pure zinc. The spraying process can, of course, be employed on material which is already erected or which is too large to be handled by any of the preceding processes. Each process has, likewise, certain individual disadvantages, and these may be best referred to when considering the working of the processes.

Hot-Dip Galvanising. In the hot-dip process the parts are first cleaned by pickling or sand-blasting and dipped into a flux, usually ammonium or zinc chloride. They are then immersed into a bath of molten zinc, withdrawn, and the excess of zinc shaken or rubbed off. It is sometimes the practice to have the flux as a supernatant layer on the surface of the molten zinc, and the material is fluxed in passing through it prior to coming into contact with the zinc. This procedure also prevents the oxidation of the zinc at its surface, and thus helps to maintain the cleanliness and purity of the bath. This process is capable of giving reasonably good results, but, as generally worked, however, it has several objectionable features. The zinc usually employed is, of course, the commercial variety, spelter, and it contains tin, lead, iron, and often cadmium as impurities, the percentage of which tends to increase as the bath is worked, particularly with respect to iron. Iron is attacked by molten zinc, and consequently the galvanising tank and the treated metal itself both contribute to an ever-increasing iron content. After this has reached a certain value, an alloy of zinc and iron separates out and settles on the bottom of the tank. To prevent this from becoming burnt on to the vessel, lead is sometimes added to the bath and, being heavy, floats this alloy on its surface and facilitates its removal. This reduces, no doubt, the difficulties in the operation of the bath, but it is not conducive to the production of a pure zinc coating, nor is the addition of tin or of aluminium which is sometimes made to obtain a smoother and more attractive-looking coating. In addition, there forms on the surface of the molten zinc a scum of the oxidised metal and other impurities through which the articles must pass before they meet the zinc. This scum both contaminates the coating and prevents its even distribution. It may readily be understood, then, that the coatings usually produced by the hot-dip process consist of a very impure zinc and often contain included extraneous matter and, as such, are the more readily susceptible to corrosive influences. Still another objection lies in the fact that the flux which is necessary, and which is usually composed of hydrochloric acid and zinc chloride or ammonium chloride, is expensive and traces of it are frequently left on the articles treated, stimulating the subsequent removal of the zinc. In nine cases out of ten, the presence of chloride can be detected in galvanised coatings.

Other bad features of the hot-dip process are that it is economical only when worked on a large scale and continuously. There is often a considerable wastage of zinc, and the coating is not one of pure zinc but contains more or less of an iron-zinc alloy, and it is generally supposed that the solution pressure of such an alloy in contact with iron and other impurities is greater than that of the pure zinc and its corrosion or removal under adverse conditions would be the more rapid in this event. The efficiency of a zinc coating depends upon its purity, continuity, and thickness, and the latter is probably of the least importance. The relative merits of the various processes for applying zinc may therefore be judged on the basis of the purity and perfection of the coatings they yield. Improvements in the hot-dip process lie in the introduction of harmless or non-corrosive fluxes and in keeping the bath of zinc as pure as possible. Much work has been done and is still in progress in this direction, though the process is itself of such a nature that it is improbable that a very pure zinc coating, applied in this way, will ever be a commercial possibility.

Sherardising.—This process of applying protective coatings of zinc was invented by Sherard Cowper-Coles about 1900, and since 1908 has been increasingly applied to the treatment of a large variety of small articles, such as screws, bolts, and intricate castings, etc., which cannot be dealt with by the hot-dip process. Sherardising consists in packing the articles with zinc dust into drums, which are then placed in a small furnace, usually gas-heated, and either continually rotated at a slow speed by power or turned by hand through about 90° at frequent and regular intervals. The articles should, of course, be first cleaned to remove dirt, grease, and scale, and the heating of the drums is continued at the correct temperature and for the proper length of time, after which they are allowed to cool, opened, and the articles separated from the zinc dust by emptying on to a screen. The process is not applicable to large material such as sheet metal, etc., but pipes and similar goods may be fairly conveniently dealt with.

The advantages of this process over the one just dealt with are that a perfectly uniform coating is produced, and that it is alloyed with the surface of the protected metal. Further, if the process is correctly carried out and controlled, the surface layer of the coating consists of pure zinc. The temperatures employed are considerably below the melting point of the zinc, and are therefore much lower than that required by the hot-dip process, and as also there need be but little wastage of zinc, the sherardising process is cheaper than hot galvanising, and it can, moreover, be worked intermittently with no loss in economy. The main disadvantage in the sherardising process is that, unless it is very carefully controlled, both with regard to the temperature and to the free zinc content of the dust used, very indifferent results may be obtained. It has also been claimed that no dimensional increase in the treated material is occasioned and that, therefore, parts may be machined and threaded, etc., prior to sherardising. Ordinarily this is the case, since, although there is a slight increase in size, it may very often be disregarded, but, in the case of really small screws and pins, etc., and similar articles whose dimensions must be accurate to within very small limits, it will be found that their assembly after treatment is impossible unless some allowance has been made to compensate for the slight dimensional increases caused by the addition of the zinc.

The production of satisfactory coatings by this "Vapour Deposition" process, as it is sometimes called, requires a knowledge of the relative effects of the temperature, the metallic or free zinc content of the dust, and the time on the quality of the coating. There appears to be little doubt that the coatings consist of an alloy or alloys of iron and zinc, and it would also appear that the permanency of the protection afforded to the treated material is considerably influenced by the proportion of the former metal, iron, in the coating. The iron contents, resulting from varied conditions such as those of temperature and metallic zinc content of the dust, have been found to range from as little as 4 per cent. to as much as 45 to 50 per cent., and it has been stated that, in certain cases, the coating is composed of as many as four distinct zinc-iron alloys. This iron content is a function of the temperature employed and also of the free zinc content of the dust used. It has been recorded that with a dust containing 18 per cent. of free zinc the iron content of the coating is about 22 per cent., whilst with a dust containing 42 per cent. of free zinc, the iron content is about 11 per cent. It is generally accepted that the durability of the coatings decreases steadily with increase in the iron content, particularly when this exceeds about 10 or 11 per cent. The effects of temperature and metallic zinc content of the dust are somewhat difficult to anticipate because of the lack of definite and complete knowledge of the solubility relations of iron and zinc. The existence of the alloys Fe_5Zn, Fe_2Zn, $FeZn_7$, $FeZn_3$, and $FeZn_{10}$ seems, however, to have been fairly definitely established by different workers, though in regard to the latter there is a difference of opinion as to whether it is really a compound or a solution of zinc in $FeZn_7$. Evidence would indicate a definite compound, since solid solutions are homogeneous and tough (viz. most industrial alloys), whereas the material represented by $FeZn_{10}$ has a definite crystalline structure and is very brittle. The occurrence of a considerable number of definite zinc-iron compounds seems very probable, and it is clear that the exact nature of the alloys which may compose a sherardised coating is, at present, difficult to determine, but the knowledge that brittle and crystalline alloys of this kind can exist, alloys which, moreover, expand and crumble on cooling, is sufficient to emphasise the necessity for exercising very strict process control in order that the materials shall be treated under conditions which have proved to give the most satisfactory results.

The iron content of the sherardised coatings is dependent upon the temperature and on the free zinc content of the dust. Some authorities state that the higher the temperature the greater is the percentage of iron in the coating. This is not definitely proved, however, but there is no doubt that increases in temperature do effect an increase in the amount of iron up to a certain point. Further increases of temperature have been observed to effect a reduction in the quantity of iron, but the surest way to avoid a high iron content is to use a dust which is rich in free zinc. The higher the percentage of free zinc, the lower is the iron content of the coating produced and, further, the lower is the temperature necessary to sherardise the material. With the higher temperatures required by dust of low free zinc content, the coating will consist of alloys rich in iron, but with dust of a high free zinc content, and the consequent lower temperature, the coating will consist of probably one alloy only, rich in zinc and with a film of pure zinc on its surface. This type of coating gives a more permanent protection than does the former type, which may contain a number of different alloys and have a complex structure, the electrical behaviour of which will be conducive to its more rapid removal. Such coatings are poorly resistant to exposure to the atmosphere, they "weather" badly, whereas coatings rich in zinc usually turn a deep grey and finally black on exposure. Good weathering properties are exhibited only by coatings which contain less than 12 or 11 per cent. of iron. If the iron is in excess of this amount, the articles soon become covered with a red iron oxide which quickly penetrates to the underlying metal.

Normally, the iron in the coatings originates from the treated material itself, and we have seen how it may adversely effect the quality of the protection afforded. Any iron which may be present as impurity in the zinc dust appears to have an even worse influence, as little as 0·5 per cent. of iron in the dust will discolour the coating, and in dust which has been used several times the iron may amount to 3 or 4 per cent. The coating resulting from treatment with this kind of dust develops a red colour almost immediately when it is exposed to moisture, and a heavy red deposit is formed which penetrates to the protected metal in a very short time.

Several theories have been put forward to explain the formation of the coatings produced by the sherardising process, but none of them appear to be entirely satisfactory. It has been suggested that magnetic oxide of iron is first formed on the articles and is then reduced by the zinc dust, resulting in the formation of zinc oxide and a zinc-iron alloy. This cannot be accepted, since it has been shown that sherardising is more readily effected in a vacuum, *i.e.*, in the absence of the oxygen necessary for the production of the magnetic oxide. The vapour theory is more popular, though there are many objections to it. It assumes that the slight, though appreciable, vapour pressure of zinc at the temperatures employed is sufficient to allow enough zinc to condense on the iron to form the alloy. This vapour pressure is less than 0·1 of a millimetre, and supposing zinc is condensed on the iron, the alloying of the two materials is not thereby explained. Again, the articles are sherardised only at the points of contact between them and the zinc dust, and it has been shown that a space of 0·001 of an inch round the material is sufficient to prevent sherardising. This should not be the case if the vapour theory were wholly correct. The most reasonable way of explaining the process would appear to be the one in which the chemical properties of the zinc, together with one or two fundamental principles of chemical reaction, are considered. Compared with the other common metals, zinc is chemically active, and this property is shared by the other two metals, mercury and cadmium, of the subdivision of the periodic group to which zinc belongs. The chemical activity of mercury is well known, and zinc comes next to mercury in order of activity. We can predict, from their positions in the periodic classification of the elements, that zinc and cadmium have similar, but less pronounced, properties to mercury, and this is actually the case. Mercury, for instance, alloys with many metals in the cold, but there is only one metal (gold) with which zinc alloys in the cold, and cadmium does not form any alloy at the ordinary temperatures. Therefore, whilst the slight vapour pressure of zinc may not be without effect in the sherardising process, the inherent chemical activity of the metal is probably the chief factor, particularly when viewed in conjunction with contact action. Generally speaking, the more finely divided the material, the more active it is, and this is especially apparent in the case of many metals, for instance, pyrophoric lead and powdered aluminium. The more finely divided the zinc, the closer is the contact that can be obtained between it and the articles treated, and intimacy of contact is a factor which also greatly facilitates chemical action. It has been shown that the coarser the zinc dust the more difficult is the sherardising process. It would appear, therefore, that the production of the coating may be regarded as due to the chemical activity of the zinc, which is increased by its state of fine division and the intimacy of contact maintained between it and the material treated. Diffusion will also undoubtedly exert a considerable influence in producing and determining the extent of the penetration of the alloy. If the property of zinc which enables it to form compounds with other metals is ignored, it is not easy to imagine how the reactions which take place between the iron and the zinc in sherardising could occur below the melting point of the zinc.

The sherardising process may be summed up as follows:

(1) The coating produced consists of a single alloy with a film of pure zinc on the surface when the process is correctly worked.

(2) Poor quality coatings are those rich in iron and whose structure is complex.

(3) The exact nature of the alloys formed is not fully established.

(4) The iron content of the coatings is a function of the temperature and of the purity of the dust used.

(5) A dust having a high metallic zinc content will give the most permanent protection.

(6) The temperature employed should be as low as possible.

(7) When properly produced, a sherardised coating offers excellent resistance to atmospheric corrosion.

(8) The production of the coating is the result of contact action between the iron and the chemically active zinc.

The Plating and Spraying Processes.—The electro-deposition of zinc immediately suggests two very decided advantages over the hot-dip and vapour deposition processes, (1) it can be carried out in the cold, and (2) it deposits a coating of exceptionally pure zinc. It is comparatively recently that the satisfactory electrolytic deposition of zinc has been possible on a commercial scale, but the fact that this process appears to be finding extended applications is significant. Several authorities report favourably on the behaviour of plated zinc coatings compared with those obtained by other means, and a considerable amount of work has been done to improve upon the very fair coatings now produced. In common with the majority of plating processes, there are many varied formulæ for the zinc vat solutions and for the electrical conditions to be maintained during the actual deposition of the metal.

Zinc plating is, unfortunately, not one of the most straightforward of plating processes, and whilst it may not be questioned that very good and satisfactorily resistant coatings can be produced by it, it is a process which none but an experienced and practical plater can control on a commercial scale. When properly carried out, the result is a smooth, uniform, and non-porous coating, the weight of which can be predetermined at will. On the other hand, it is extremely easy to produce coatings which are very porous and in which impurities from the plating bath are included. Also, unless great care is taken, there is a strong tendency for the zinc to build up on the more prominent parts of the articles, the undercut of recessed portions of the surface receiving merely a film or flashing of zinc. In fairly large articles, this tendency can be much reduced by building up the anodes from pieces of zinc, so that they present in contour a rough and reversed counterpart of the materials being plated. A further serious disadvantage of electro-zincing is that after the coating has reached a certain thickness it is very liable to develop a rough and crystalline surface. These objections are due, however, almost entirely to the lack of technical knowledge on zinc plating, and the process is worthy of investigation and improvement. It is cheap, readily standardised, and is capable of producing a protective coating superior in its resistant qualities to any of those applied by the other processes available.

The spraying or Schoop process is a novel one, but, as regards its use for applying zinc, it does not appear to have any special merit which would give it preference over the other methods, except, perhaps, that it is the most readily applicable to large material and structures. The apparatus consists of a sort of pistol to which are connected three flexible tubes, one for oxygen, one for hydrogen, and one for compressed air. The gases, oxygen and hydrogen, are burnt inside the pistol, and zinc, in the form of wire, is fed into the apparatus by means of a suitable device, operated by a small air motor. On reaching the flame of the burning gases, the zinc is immediately fused and a strong blast blows it from the nozzle in the form of a spray which is directed on to the material being zinced. The velocity of the minute zinc particles composing the spray is said to be about 3000 feet per second, and a few inches from the nozzle the temperature of the spray is so low that it may be directed on to the hand for a few seconds. It is therefore assumed that when the solid zinc particles hit the surface of the metal against which they are directed, the heat of the collision is sufficient to liquefy them and so ensure their adherence. A zinc coating of any thickness can be obtained in this way, but it is porous and costly. As a method for applying metal coatings generally, however, the Schoop process would appear to have a wide field of useful service.

Other Metallic Protective Coatings.—Apart from the treatment of roofing material, the use of tin is mainly confined to the coating of cans and domestic utensils. It is not employed because it is electro-positive to iron; being, in fact, electro-negative; but because its solution pressure is so very low that it is extremely resistant to corrosion. It may be applied in a similar manner to zinc by a hot-dip process, but it appears to be a matter of great difficulty to produce, at any rate economically, a coating which is perfectly non-porous. Pin holes seem to be a characteristic of this kind of coating and therefore seriously detract from its usefulness, particularly when it is remembered that of the two metals, iron and tin, the former is the electro-positive one. Tin may also be applied electrolytically, though the method is not very extensively used. Tin is a difficult metal to deposit satisfactorily, and the remarks made in connection with zinc plating may be extended, with but little modification, to the case of tin.

Copper and nickel are both applied by electrolysis, and although the processes call for a considerable amount of skill, the coatings produced are, for many purposes, without rivals. Like tin, copper is electro-negative to iron, but it resists most ordinary corrosive influences excellently, chiefly because the products of its corrosion protect it from further attack. Even should the perfection of a copper coating become damaged, its protective action need not necessarily cease. It has been observed that in cases where a certain amount of corrosion has occurred on the underlying iron, this has been arrested by a thin film of copper which plated out from the electrolyte onto the iron underneath the rust. So long as this film remains intact, it behaves similarly to the original coating. Copper is deposited from two kinds of baths, acid and cyanide. The first is simply a solution of copper sulphate containing a small amount of free sulphuric acid, and is used for materials which are not attacked by the dilute acid. Ferrous materials cannot, of course, be plated in this solution. The cyanide bath is prepared by dissolved basic carbonate of copper in a slight excess of potassium cyanide: it gives an excellent deposit quickly, and is a much simpler bath to work than is the acid bath. A certain amount of "copper-clad" steel is made by welding or alloying copper on to the articles. For material which is exposed to the atmosphere it is difficult to improve upon the protection which a properly applied coating of copper will give.

The use of lead in obtaining protective coatings has been very limited up to now. Perhaps the best known method of applying it is the Lohmannising process which consists in immersing the materials in a bath of molten lead or of a lead alloy. The secret of the process would seem to be in the use of suitable fluxes. An alloy of tin and lead is used in the treatment of metal plate, but the use of lead is very limited and there does not appear to be any recorded observations of its behaviour as a protection.

The Use of Aluminium. Calorising. An account of this process, which is primarily directed towards the prevention of the oxidation of metals subjected to high temperatures, and whose destruction thereby is not the result of corrosion as we have defined it, must be given for several reasons. It will be remembered that a liquid conductor is essential to ionic oxidation or corrosion proper, whereas the destruction of metals at high temperatures is due to their direct or molecular oxidation and is independent of an electrolyte, but since we are so closely concerned with the preservation of material, and since, also, the calorising process has acquired a certain, if secondary application, in the protection against corrosion proper, its inclusion is justified. It is the only process which, up to the present time, has been successful in affording protection against high temperatures.

The calorising process was introduced by Van Aller in 1911 (*Chemical Age*, VII, 163, 1922), and was developed and patented by the General Electric Company of Schenectady, U.S.A. A plant is owned in this country by the Scarab Oil Burning Co., Ltd., of London, and the process would appear to have proved a successful and economical method of protecting, not only iron and steel, but also copper and brass and other metals whose service entails exposure to abnormally high temperatures. Although its introduction is so recent, its use has extended beyond its original application to electric heating work, to a large variety of material, such as iron and steel retorts, annealing boxes, furnace parts, pyrometer tubes, oil-cracking stills, condenser tubes, gas- and oil-engine parts such as valves and piston heads, preheating coils, coke oven parts, ceramic apparatus, vitreous enamelling furnaces, oil burners, mechanical stokers, kilns, muffles, furnace linings, and generally to material in which failure is attributed to the action of heat alone.

The process is very similar to that of sherardising, which has already been dealt with. It consists in heating the material in a retort under a reducing atmosphere and in contact with a mixture of aluminium oxide and finely divided aluminium, analogous to the sherardising powder composed of zinc dust and zinc oxide. A current of hydrogen is passed through the retort during the process and the articles are, of course, first thoroughly cleaned to remove grease and rust, or scale. The temperature employed in the operation is about 870° to 900° C. and there results an alloying between the metallic aluminium and the surfaces of the treated material. The depth to which the alloying penetrates can be controlled by varying the duration of the treatment and may range from a few thousandths of an inch to the complete permeation of the entire mass of the metal. It is regulated according to the conditions under which the treated metal has to serve. If excessive heat only has to be considered, a very thin penetration of the alloy is sufficient, but if the conditions of service are abrasive or otherwise mechanically severe, a much thicker or deeper penetration is aimed at.

FIG. 14.—SECTION THROUGH CALORISED MATERIAL.

The aluminium enters into solid solution with the metal, and the protection it affords is due to the formation of a surface layer of aluminium oxide or alumina which prevents the oxidising gases from coming into contact with the metal beneath it. Immediately below the layer of alumina is one of pure aluminium, then there comes a relatively thick layer of the aluminium-iron alloy, and below this is the base metal, fig. 14. The alloy is very hard, and should the outer coating of alumina be removed or destroyed by any means it is instantly replaced by the oxidation of the underlying aluminium. The protection is therefore regenerative and continues

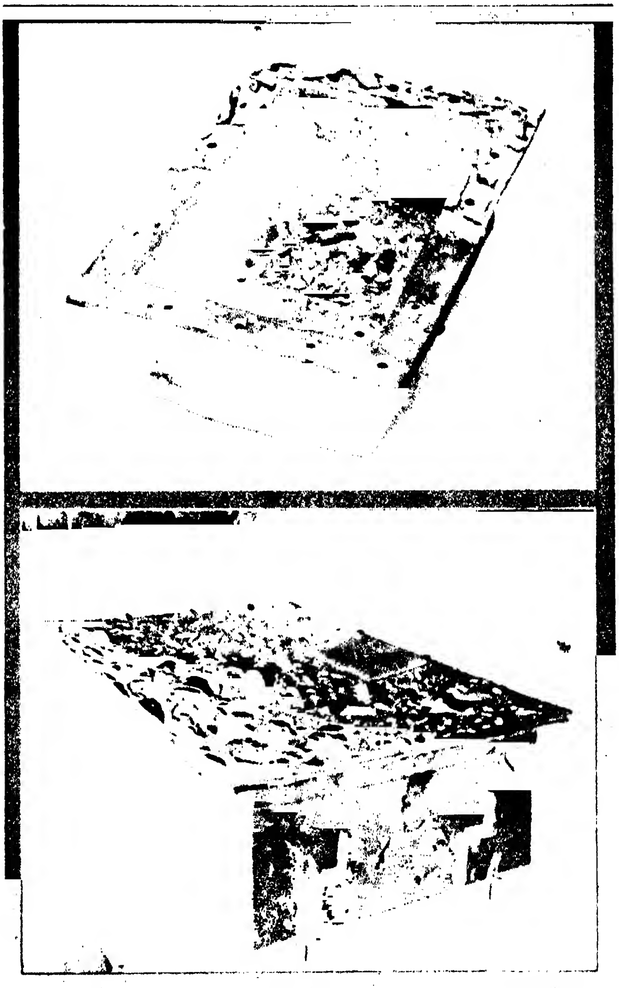

FIG. 15.—ANNEALING BOXES SHOWING PROTECTION AFFORDED BY CALORISING.

to be so until the abrasion has penetrated the entire depth of the alloy. Fig. 15 illustrates very clearly the protection afforded in the case of annealing boxes. The box shown in the upper portion of the figure was cut in two; one half was calorised, and then welded on to the uncalorised portion. After 30 hours' exposure to a temperature of 820° C. the conditions of the two halves offered the striking contrast shown. In the second case, a small rectangular piece was removed from the annealing box cover, calorised, and replaced. Two heating periods of 5 hours each at 820° C. resulted in a considerable burning or scaling of the uncalorised metal whilst the calorised portion remained undamaged.

It is stated that calorised material will withstand a temperature of 900° C. almost indefinitely and, compared with untreated material, will last from five to twenty times as long under temperatures from 900° to 1000° C., and from two to five times as long under temperatures from 1000° to 1100° C. Untreated metal commences to oxidise appreciably at 600° C., and at 800° C. its deterioration is very rapid. Furnace gases generally contain carbon dioxide and sulphur dioxide, and, at the temperatures prevailing, have a very rapidly destructive action on unprotected metal. Calorised metal, however, is said to be unaffected by such conditions.

FIG. 16.—CALORISED AND UNCALORISED PIPE UNIONS.

Most metals, iron, steel, copper, nickel, brass, and monel metal, can be successfully calorised and, in general, wrought, pressed, drawn, forged, and rolled material, being free from surface cracks and imperfections or inclusions, etc., may be more successfully treated than cast metal. White or malleable cast iron has also proved preferable to grey cast iron for this treatment. Although calorising does not produce a coating that is sharply defined or that can be detached by chipping or flaking, all operations such as bending or other forms of working must be carried out prior to calorising, but if this is impossible, it may be done with the calorised material heated to bright redness. Threading should be done before calorising and the threads chased afterwards if necessary. The success of the process depends wholly on the preservation of an unbroken aluminium oxide surface and of the material necessary for its renewal. For this reason, all processes such as cutting, riveting, drilling, machining, and welding are preferably performed on the uncalorised metal. With regard to welding, it may be pointed out that calorised metal is very difficult to weld because of the persistent formation of the alumina film.

Calorising was not originally intended to protect metals from corrosion, yet it has been found that in many cases it does actually give this protection. Brass and copper, when calorised, are much more resistant to brine, and certain acid solutions and calorised ferrous materials also offer increased resistance to many corrosive influences. Calorised tubes have been employed in condensers with very satisfactory results, and electrical material of treated copper appears to be quite unaffected by atmospheric corrosive influences.

For those classes of material which are unlikely to suffer much mechanical damage and in which protection may consequently be efficiently afforded by a thin penetration of the alloy, a dipping process is available which gives good results at a low cost. The limitations of the calorising process are comparable with those of others which employ high temperatures to produce protective skins or layers. Warpage of the material is a probability which must be taken into consideration together with the likely modifications which may be effected in the mechanical properties of the metal. Generally, the process is equivalent to annealing. One of the chief recommendations of the process would appear to be that for the expensive heat-resisting alloys may be substituted the comparatively cheap calorised iron or steel. Fig. 16 shows a calorised and an uncalorised pipe union after 50 hours' exposure to a temperature of 1000° C.

CHAPTER XIII

PAINTS AND ALLIED COATINGS

PAINTS and like materials are so common and familiar that they are apt to receive but minor consideration with regard to the protection of iron and steel from corrosion, and the fact that they have a definite function in this connection may often be overlooked. Yet the extent of protection afforded to practically all structural materials is dependent upon the suitability and quality of the paints which are applied to them. Plating, galvanising and the other protective measures which have been dealt with up to now are of great value and are widely used, but they are not universally applicable. It would not be practicable, either from the point of view of cost or of the necessary plant, to plate, sherardise, or Bower-Barff the large girders, columns, and other components of steel and iron structures, and there are numerous other instances in which it would be too costly to apply such finishes, and in many cases, even if this were carried out, it would be necessary to employ a final paint finish for the sake of appearance and further protection. The importance of paints should not, therefore, be relegated to a secondary position in the consideration of protective coatings. They are often the only alternative by which protection can be given to iron and steel.

In order that a paint shall provide an efficient protection to the metal to which it is applied, it must conform to two essentials: (1) it must be impervious to moisture and, (2) its ingredients must be neutral or opposed to corrosive influences. From a consideration of the theory of corrosion, it may readily be conceived, for instance, that pigments which are basic in character and which, in the presence of moisture, tend to increase the concentration of hydroxyl ions, may be advantageously employed in a paint and will exert an influence in the right direction, even when the paint film is abraded or otherwise damaged, whilst pigments of an acid character, or which are liable to develop acidity on exposure, will prove unsatisfactory and detrimental, particularly if used in a priming coat. A good protective paint should exclude water completely, and should contain some ingredient which will prevent the formation of hydrogen ions.

Paints consist of pigments or colouring matter suspended in oil, and usually contain also certain proportions of driers and thinners such as benzine, turpentine, etc. There are two principal methods of preparation, the first, and probably the better, is to mix the predetermined proportions of pigment and vehicle (oil) together and then pass the mixture several times through a paint mill. This method ensures a paint in which the ingredients are thoroughly incorporated and in which they are most likely to be present in the correct proportions. The second method consists in grinding the pigment together with a portion of the oil sufficient only to produce a paste which is easily handled by the paint mill. The "concentrated" paint is afterwards mixed as desired with more oil, and driers and turpentine, or other thinner, are then also added.

The Essential Properties of Paints. A paint which is intended for application to structural material should be impermeable to rain and moisture and should remain sufficiently elastic to be unaffected by the expansion and contraction of the metal covered by it. The elasticity of a linseed oil film itself is not permanent, but by the proper control of the proportion of pigments this property can be maintained. In order that the impermeability or excluding property of paint films may be enhanced, it has been suggested that the pigments contained in them should be graded in particle size and that a paint which contains both fine and relatively coarse pigment particles is superior to one in which the pigment particles are of a uniform size.

It is very desirable that paint used on structural material shall have a good hiding power or opacity. Proper concealing of the metal surface is essential both from a protective and a decorative point of view. The opacity affords greater protection from the sun and is determined by the difference between the refractive indices of the pigment and the vehicle. The greater the difference between the indices of refraction of these components of the paint, the greater the opacity of the paint.

Pigments are classified in the paint trade according to their behaviour towards the vehicle in which they are suspended. "Inert" pigments are those which are without action on the oil but whose opacity is relatively poor. Other pigments cause saponification of the oil and result in the destruction of the paint film. This "active" class includes pigments which may have excellent hiding power but their pronounced alkalinity off-sets this and leads to the development of discoloration and other defects.

Many pigments are adversely affected by industrial atmospheres, containing, for example, sulphurous gases. Certain varieties of white lead (basic carbonate) are readily affected and discoloured owing to the formation of the black sulphide of lead. On the other hand, zinc oxide and the basic sulphate white lead are practically unaffected by such conditions. Since it is not desirable that white pigments should discolour in service, they should therefore be chosen from a consideration of the conditions under which they have to serve. Lithopone, though perhaps the most intensely white of all pigments, is not permanent under exposed conditions and is very liable to darken.

The spreading quality of the paint should not be either too high nor too low. This property is entirely due to the particular pigments used; some have a very poor covering value, whilst others go to the other extreme, and as a result the paint may be applied so thinly that it offers but a poor resistance to atmospheric influences although appearing perfect visually. A combination of pigments of each type is usually considered advisable, a reasonable spreading power is obtained, and excessive thinness of the film is automatically avoided. In order to strengthen and toughen a paint film, asbestine and talcose are frequently used as reinforcements. Asbestine, or magnesium silicate, has needle-shaped particles, whilst those of talcose, or aluminium silicate, are flake-like, and they are also of use in conjunction with certain white pigments which alone have undesirable properties. They possess the property of preventing the sedimentation or settling of heavy pigments and are much used to correct this tendency.

Paint Materials.—In order to decide upon a suitable paint for purposes of protection, it is necessary to have some knowledge of the various materials used in the preparation of paints. The basis of most paints is linseed oil. This is obtained from the seeds of the flax plant by either of the two processes in vogue, viz., by crushing and pressing or by the solvent extraction of the oil from the seeds with naphtha. After a process of purification, the oil is treated to increase the rapidity with which it dries. The pure oil, on exposure to the air, slowly absorbs oxygen and at the same time thickens until finally a tough, elastic skin is produced. This final product is known as " linoxyn " and its composition is uncertain. The drying property is the one which renders linseed oil especially suitable for a paint vehicle, the film produced is fairly tough and is not too readily damaged mechanically, and it forms a good support for the colouring pigment.

For practical purposes, however, the pure oil dries too slowly, and it is therefore " boiled " or heated to 400° to 500° F., which results in an oil which dries much more quickly. The addition of certain metallic salts, such as those of lead and manganese, to the heated oil has the same effect. The present method of treating the oil is somewhat different, and gives a product which is considerably lighter in colour, a property which is very often desirable. A small portion of the oil is heated to a high temperature with a metallic oxide such as litharge and an oil drier, or siccative, is obtained. The siccative is then dissolved in turpentine or benzine and added to the bulk of the oil at a temperature of about 110° C. Besides giving a superior product, this method is more economical in time, labour, and fuel; paints can be made up with raw oil and a proportion of drier added, or with a mixture of raw and boiled oils, plus also a quantity of drier.

A paint compounded with raw linseed oil alone would dry so slowly that it would be quite unsuitable for practical use, though excellent coatings would be produced in time. Hence the addition of a certain proportion of driers is necessary, but it should be remembered that the action of the drier continues after the paint has dried, and ultimately tends to destroy the film. Driers should be used with discrimination therefore; both as regards their nature and quantity they have considerable influence on the durability and quality of the paint; and it is clearly false economy to shorten the useful period of service of the paint for the sake of a little gain in the drying time. The oxides of lead and manganese are the two materials which are most generally used in the preparation of siccatives. Their behaviour differs: manganese has a rapid action, and tends to harden or dry the surface of the film more quickly than the underlying portion; with a lead drier, the hardening proceeds more uniformly throughout the film. Lead, in consequence, usually predominates in quantity over manganese. Red lead appears to impart a more brittle character to the film, whilst litharge gives an elastic film. Other siccatives are made by melting resins with the oxides of lead and manganese and are known as Japan driers. They are very rapid in their siccative action, but are not so satisfactory as the "oil" driers, *i.e.*, those made from the oil itself.

Other oils which have found application in the manufacture of paints as adulterants or substitutes for linseed oil are, China-wood or Tung oil, Soya-bean oil and Poppy-seed oil. China-wood oil can be prepared so as to yield a hard and glossy film which is elastic and gives a paint which dries well in a damp atmosphere. It appears to possess desirable qualities from the standpoint of protective coatings, and is becoming popular as a vehicle for marine and waterproof paints. Soya-bean oil is also being used successfully in the preparation of paints; it is very similar in most respects to linseed oil, and the adulteration of the latter with it is very difficult to detect.

The common adulterants of linseed oil are mineral oils and turpentine or turpentine substitutes, rosin and rosin oils, fish oils, and cotton-seed oil. Turpentine is the most useful thinning material for paints, it increases their covering powers and adds to the ease with which they can be applied or "worked," and has also the effect of increasing the speed with which the paints dry. It is the product of the distillation of the sap of several varieties of pine trees (the residue left in the still after distillation being rosin). There are a number of varieties of turpentine, but they differ principally in certain physical properties, such as specific gravity, etc., and not in composition. The pure material evaporates slowly and steadily, and leaves no stain on the surface from which it dries: inferior qualities leave a stain. Owing to its rather high price, substitutes have been proposed, and several materials are available as such or as adulterants. Of these, the best are light mineral oils obtained during the processes of refining petroleum, etc., and in many essential respects they are very similar to and as good as turpentine.

Pigments. - The suitability of a paint for protective purposes is largely determined by the character of the pigment it contains. Practical experience has indicated that certain pigments are superior and that others are inferior in this connection, and a considerable amount of work has been carried out with a view to investigating and correlating the behaviours of different pigments. Thus it has been found that certain of them possess the property of exciting electrical action and stimulating corrosion when in contact with iron, whilst others show an inhibitive tendency. As a result, the commoner pigments have been classified as stimulators and inhibitors, those of a variable or indefinite behaviour being grouped under the heading of "indeterminates" (*Proc. Amer. Soc. Testing Materials.* **10.** 1910). (See page 160.)

The behaviour of a pigment is determined, not only by its composition, but also by the method of its preparation and the impurities it may contain. Chromic acid compounds, for instance, would rightly be regarded as belonging to the inhibitive group, and in the majority of cases they do, but in others it has been found that instead of possessing inhibitive properties, they are actually stimulative. Some grades of Prussian blue are manufactured in such a manner that it is impossible completely to free them from traces of acid, and these grades of this pigment behave in a manner which necessitates their inclusion in the stimulative group. In addition

Inhibitors.	Indeterminates.	Stimulators.
Zinc lead chromate	White lead (*a*)	Lampblack
Zinc oxide	White lead (*b*)	Barium sulphate (*h*)
Zinc chromate	Blue lead (*c*)	Ochre
Zinc barium chromate	Lithopone	Bright red oxide
Zinc lead white	Orange mineral (*d*)	Carbon black
Prussian blue (inhibitive)	Red lead	Graphite No. 2
Chrome green (blue tone)	Litharge	Barium sulphate (*i*)
White lead (Dutch process)	Venetian red	Graphite No. 1
Ultramarine blue	Metallic brown (*e*)	Prussian blue (*j*)
Willow charcoal	Calcium carbonate (*f*)	
	Calcium carbonate (*g*)	
	Calcium sulphate	
	China clay	
	Asbestine	
	American vermillion	
	Chrome yellow (medium)	

(*a*) Basic carbonate, Quick process.
(*b*) Basic sulphate.
(*c*) Sublimed.
(*d*) American.
(*e*) Prince's.
(*f*) Whiting.
(*g*) Precipitated.
(*h*) Precipitated, Blanc Fixe.
(*i*) Barytes.
(*j*) Stimulative.

to the ease with which a pigment may dissolve and ionise in traces of moisture, thus producing an acid, neutral, or alkaline electrolyte, as the case may be, the purely electrical properties have also considerable significance. A pigment which is a good conductor can facilitate electrolytic action, and, since the linseed oil films in which the pigments are suspended are always more or less porous and can absorb water and carbon dioxide, such conducting pigments will co-operate with the other corrosive influences. An insulating pigment, on the other hand, will exert an opposing force to these influences. Conducting pigments belong, therefore, to the stimulative group and insulating pigments to the inhibitive group.

Apart from their individual characteristics, pigments may also considerably modify the properties of the oil film. As already pointed out, linseed oil films are appreciably porous, and moisture and atmospheric gases can penetrate them to the underlying metal surface. The ensuing corrosion is detrimental to the metal and the paint alike, and the deterioration in the latter is usually announced by the appearance of blisters which mark the spots at which corrosion is proceeding. The addition of gums or varnish to the paint may correct this porosity to a large extent and produce a film which is much more impermeable to moisture, or, in other words, is a better excluder. The action of the gum is to fill or close up the pores in the oil film. In addition to the excluding property, however, there is another which is equally desirable, and which may not be conferred by the use of gums, namely, the water-shedding property or the ability to remain unwetted. Certain pigments impart both these properties to the oil film, so that it both prevents the penetration of moisture and dries rapidly after being wetted. Non-water-shedding paints hold the water on their surface and tend to absorb it, and this ultimately leads to the disintegration of the paint, accompanied, of course, by the corrosion of the iron or steel beneath it. The size of the pigment particles has a considerable effect in reducing the permeability of the film; the more finely divided it is, the greater the reduction in the number and size of the pores.

With regard to the compounding of paint which contains one pigment belonging to the inhibitive group and a second pigment belonging to the stimulative group, the resultant behaviour of the coating, from the point of view of the protection afforded by it, is a matter of conjecture, and a decision can be reached safely only by actual practical experiment. It might be reasonably anticipated that the presence of an inhibitive pigment would reduce the adverse activity of a stimulative pigment, and that if the proportion of the former were sufficiently large, might even completely obscure the corrosive tendencies of the stimulator. The question may, however, be equally well regarded from another standpoint, analogous to that of the strength of a chain being that of its weakest link. If the metal is subjected to corrosive influences and the paint covering it contains materials of which one co-operates with these influences whilst the other contends against them, it is always possible that in certain localities or under certain conditions the forces for corrosion may overcome those opposed to the process. In such an event a breakdown of the inhibitor's action would occur, not generally, but probably over localised portions of the surface, and consequently the corrosion would tend to assume the form of pitting.

The Application and Choice of Paints. From the foregoing, certain conclusions may be drawn as to the correct method of using paints. For instance, a paint containing a stimulative or conducting pigment is clearly not suitable as a priming coat, that is, one which is applied directly to the metal surface. The priming coat should contain an inhibitive pigment, such as a chromic acid derivative or zinc oxide, etc., or an indeterminate such as red lead or white lead plus a smaller proportion of a stronger inhibitor. Over this may then be applied a paint designed more from an excluding or water-shedding standpoint and with less regard to inhibitive qualities.

The proper treatment of a metal surface prior to painting is a matter which is of scarcely less importance than the character of the paint itself. A point which is, in the very large majority of cases, either unappreciated or neglected, is that it is advantageous to heat the surface of the metal before applying the paint. Painters refuse to work on metal which is obviously wet, yet the fact that an apparently dry surface may cloak the presence of a considerable amount of moisture, held in the surface pores of the metal, is overlooked. Slight fluctuations of temperature only are required to cause this moisture to coalesce in liquid form and appear as "sweat" on the surface, and if this occurs underneath a paint film, it will do so to the detriment of the latter and also, of course, of the metal. The difficulties of dealing with this moisture, particularly on large structures, are fully realised, but it is probable that a blow-lamp would render effective service in many cases.

Allied to the complete removal of moisture wherever possible is the removal of rust. This should always be thoroughly cleaned away, either by means of wire brushes, scraping, or, where the size permits, by pickling, before the material is repainted. The necessity for this is obvious, rust is hygroscopic and can absorb moisture and is an accelerator of corrosion processes. Its incomplete removal is, in many cases, directly responsible for the rapid deterioration of the paint. Mill-scale is a like offender, though in this case it is considered to be sufficient to remove only the loosely adherent portions of it. Sand-blasting is a useful alternative method of cleaning surfaces for repainting; it is quicker and more thorough on intricate surfaces, and quickly removes old paint and rust and gives the metal surface a good condition in which to receive the new coating. Contrasted with the older methods of hand cleaning and painting, particularly of large surfaces, the sand-blasting, if followed up by paint spraying, offers a more rapid, efficient, and economical procedure, especially on rough and intricate surfaces. Paint spraying (pneumatically) gives the very desirable uniformity of distribution.

All oil and grease should, of course, be removed, and in the case of new material received from the manufacturers, it is always necessary to remove the shop coatings which are given to it to protect it during transit. There are numerous varieties of shop coatings, and their behaviour towards a superimposed coat of paint is problematic. They may not be perfectly dry when the material is received, or they may have suffered mechanical damage in transit and the resultant corrosion already established. They may be very porous and therefore saturated with atmospheric moisture and carbon dioxide, etc., acquired during shipment. Especially does this apply to coatings of linseed oil, for if such coatings are abraded and the metal is exposed, the oil accelerates the corrosion which ensues, presumably, it is supposed, by acting as a depolariser and removing the hydrogen produced by absorbing it.

In addition to general considerations, similar to the above, it must be borne in mind that no one variety of paint is universally applicable as a protective coating. A particular paint may prove quite unsuitable for use on a certain kind of metal or under certain specific conditions, such as exposure to sea-water or industrial atmospheres. The painting of galvanised metal, for instance, is regarded by the painter as a difficult proposition owing to the peculiar character of the surface of the zinc-coated metal, to which most paints adhere but imperfectly and soon blister or peel, or crack away. Large quantities of galvanised material are in use, however, and it is necessary to paint them both for decorative purposes and to give a further protection against corrosion. Different methods have been employed to confer on the zinc surface a roughness to which the paint can more readily adhere. Pickling in acids and acid salts and other mixtures have been tried in turn, but such procedures are not to be recommended either from theoretical or practical considerations. It is now considered a sounder practice to apply a priming coat of varnish containing a sharp siliceous pigment which can form a union with the metal by its " bite " and which is also closely cemented by the varnish. The desired colour may then be given by a paint which can be superimposed on this priming coat satisfactorily. Tinned metal surfaces do not present the difficulties experienced with galvanised surfaces, and any good inhibitive composition may be used as a priming coat.

The painting of marine structures and the hulls of vessels is another problem which has demanded a great deal of attention. In addition to the disintegrating action of sea-water on paints in general, it is known that the marine growths which accumulate on such structures, stimulate corrosion. Consequently the desiderata for paints for use in these cases are that they shall be good excluders, shall contain inhibitive pigments, and also contain ingredients which are obnoxious or poisonous to marine growths and which will therefore prevent their accumulation. The priming coat should contain in the vehicle a good hard-drying varnish in order to confer the necessary excluding properties on the film. Subsequent coats may have incorporated in them the "anti-barnacle," etc., material, of which several alternatives are available. Copper and arsenic soaps (made by precipitating a saponified oil with the soluble salts of these metals), corrosive sublimate, mercuric oxide, etc., are efficacious when dissolved or suspended in the vehicle. Semi-drying paints containing oxide of iron as pigment and pine tar or crude oil as vehicle, and in which an alkaloid has been included, have also been successfully employed.

A somewhat similar and also difficult problem is the protection by means of a suitable paint of the iron and steel materials used in the construction of tunnels and mines. The drippings in these situations may often be of an extremely corrosive and paint-removing nature, due to the presence in them of chlorides and other dissolved salts, etc. In tunnels, the atmosphere is frequently rich in sulphurous gases and carbon dioxide, and is also generally saturated with moisture. Such conditions call for an exceptionally good excluding paint, and the addition of gums to oil paints is therefore to be recommended for these cases equally as well as in marine paints. Refined coal tar and lime compositions, as well as bituminous or asphaltic preparations, are also useful in the dark and damp conditions of mines and tunnels.

Apart from these kinds of specialised cases, the efficient painting of material which is continuously exposed to the weather may be regarded as embodied by two main principles. First, the application of a priming coat containing an inhibitive or insulating pigment to prevent the initiation of corrosion, and, secondly, the application of a second or more coats which are designed to exclude and shed moisture and so protect the priming coat. Red lead, though classed as an indeterminate, has proved an excellent pigment for priming coats. Its particles are small and tend to settle quickly, but the addition of asbestine or barytes prevents this and also increases the adhesiveness of the paint. Zinc chromate and oxide of iron are also considered good priming coat pigments.

PROTECTIVE COATINGS ALLIED TO PAINTS

Japans and Bituminous Coatings. The japans constitute a class of material which is extensively employed in giving a "finish" to a large variety of small metal work where a durable and inexpensive coating is required. They afford a means of obtaining a good protective and attractive coating both quickly and cheaply, and several coats may be applied in a much shorter time than that required for a single coat of paint to become thoroughly dry and fit for the superimposition of a second coat.

Black japans are prepared by compounding linseed oil and asphalt, stearine pitch, coal-tar pitch, gilsonite or elaterite, etc., at a high temperature. The resulting product is thinned with turpentine or turpentine substitute and applied to the metal by dipping or spraying. The articles are then baked at temperatures ranging from 200° to 450° F., the precise temperature and period of baking (two hours and upwards) being determined by the composition of the japan. The coatings which are produced are hard and glossy and thick and are reasonably impermeable. By incorporating carbon black or lampblack in the japan, varying degrees of dull and matt finishes may be obtained. The coloured japans, or stoving enamels, consist of pigments ground in boiled linseed oil and to which are usually added a quantity of varnish gum. Their baking temperatures are much lower than those of the black japans.

The coatings produced by the baking japans are much harder than paint films and will withstand rougher handling and service. For many purposes this gives them an advantage over paints, and although they are not usually intended for service under exposed conditions, and are considered less resistant under such circumstances than good oil paints, yet they often give excellent results and protection under very adverse conditions. The baking process limits the extent of their application as well as the size of the material to which they can be applied, and the tendency of many of them to chip off under service also detracts somewhat from their merits as protective coatings. The vitreous enamels are analogous to the japans in many respects, and their sphere of usefulness is probably more limited. Their production requires excessively high temperatures, and this rules out, almost completely, their application to mechanical material. They are, however, quite impermeable, but are readily damaged or chipped They consist of mixtures of refractory materials which, on the finished articles, are virtually glasses.

The old Angus Smith process of treating iron pipes is an interesting illustration of the use of material of a bituminous character for protecting iron from corrosion. Because of their insulating or non-conducting properties, this class of material would appear to suggest itself as almost ideal from the electro-chemical theory of corrosion, and if used with discrimination and with due regard to their limitations in other respects, they justify their theoretical suitabilities as protective agents. The Angus Smith patent consisted in treating the metal by dipping it into a mixture of coal tar (from which the lighter fractions had been removed by distillation) and linseed oil maintained at a high temperature. The metal was first well cleaned and then coated with linseed oil. This was baked on to the metal and the whole then dipped, whilst still hot, into the coal-tar mixture. On withdrawal, the heat in the metal sufficed to bake on the coating thus acquired. Asphaltum or gilsonite, mixed with linseed oil or mineral oil, has also been used successfully for this purpose. Very little real advance in this process has been made, however, since it was first introduced by Smith. Sabin (*The Technology of Paint and Varnish*) has effected some improvement in the process by using a mixture of asphaltum and linseed oil heated to a temperature of 300° F., into which the cleaned metal is dipped. It is then allowed to drain until the excess of the mixture has run off, and it is then baked in an oven for about two hours at 300° F., or until the oil is thoroughly oxidised, and the coating hardened. A hard and elastic covering is produced, and it is stated that the elasticity can be controlled to any desired degree by varying the proportions of linseed oil in the asphaltum. This process has met with considerable favour in the United States for giving protection to pipe lines and buried material generally.

A further modification in the use of bituminous materials is one in which additional strength is given to the protective coating by means of a fabric reinforcement. The pipes are first cleaned and dried and then dipped into a hot bituminous compound. They are then removed and allowed to cool, after which there is wound on them strips of fabric, saturated with the hot bitumen, either in a single, a double, or a triple layer. A hard, tough, and flexible coating thus results, and, as may be imagined, is principally applied to water pipes and similar materials, which have to be buried in the ground, and which, whilst being put into service, are subjected to much rough handling whereby most other protective coatings would be seriously damaged.

Another process, employing refined coal tar, is due to Wood (*Corrosion and Electrolysis of Iron and Steel*). From 20 to 25 per cent. of quick lime is added to the coal tar to neutralise acidity, and then there is introduced into the hot mixture an equal amount of Portland or similar cement. The resulting preparation is applied hot to the cleaned and dried iron, and after allowing the first coating to cool subsequent coatings may be applied. Over the last of these, dry Portland cement is brushed on. This coating is impervious to gases and moisture, and owing to the bonding effect of the solid ingredients does not soften sufficiently to run off or flow below a temperature of about 140° F. It is therefore recommended for use under conditions where alternations of temperature occur over an unusual range and where the atmosphere is especially dangerous from a corrosion point of view.

Although these bituminous coatings are of great value, their sphere of usefulness in common with those of other protective coatings, is limited. They are all affected by exposure to sunlight and general atmospheric conditions, whether they are composed of naturally occurring or artificially produced bitumens. They undergo changes through the influence of water and light, which are detrimental to their protective qualities, and hence their application is generally limited to those fields of service from which sunlight is excluded (*Asphalts and Allied Substances*, H. Abraham). The deterioration of bituminous materials is due to the absorption of moisture, oxidation, the formation of free carbon, and the elimination of a portion of the hydrogen, and normally these actions proceed most rapidly in sunlight, the actinic rays being apparently responsible. This class of protective coating is applicable to the treatment of pipe lines and tunnel work and in certain cases where the temperature conditions are too high for other forms of paints. Ordinary tar paints, particularly those containing crude tar, should always be regarded with a certain amount of suspicion, since they are in themselves corrosive. Crude tar contains moisture always and may also contain acids, especially wood tar. These constituents can set up and maintain corrosion underneath the tar coating, and although the water and acidity can be removed, such purification is sufficiently expensive and difficult to detract from the advantages to be gained by using purified tar. Wood's process would appear to be the most reliable and economical method of rendering the tar innocuous, and it further ensures a considerable measure of non-fluidity under the sun's rays.

SUMMARY OF VARIOUS PIGMENTS

Asbestine.—Asbestine consists of magnesium silicate or ordinary asbestos ground to a fine powder. It is used chiefly to strengthen and reinforce paint films and to prevent the sedimentation of heavy pigments. It is also of value in giving " tooth " to the paint. From a corrosive standpoint it is probably neutral, neither inhibitive nor stimulative. It has little " body."

Barium Chromate.—This is produced by inter-reaction between barium chloride and sodium chromate. It is pale yellow in colour and not very good as an inhibitor, due probably to the impurities it contains.

Barium Sulphate, Barytes. Barium sulphate occurs naturally in large quantities as heavy spar. It is ground into a fine powder and treated with sulphuric acid to improve the colour. It forms the base of nearly all the lake colours and is very stable, but deficient in " body." Mixed with white lead, it provides a cheaper but inferior material to the latter, though small percentages might be conveniently added to correct the tendency of the white lead to blacken. The artificial variety, Blanc Fixe, is made by precipitating a barium salt with a soluble sulphate and is a more valuable pigment than the natural form, possessssing more " body." Both varieties contain acids, however, and are not suitable for application to iron, or at any rate, unless they have been tested. The pigments are very heavy and grind in about 10 per cent. of oil.

Blue Lead.—This pigment does not appear to be produced in this country. Considerable quantities are made in America by burning a mixture of galena and coal. The product is a sublimate and is deposited and collected in large fabric bags. It is a valuable pigment and has been recommended for marine use because of the hardness and imperviousness of the paint film which it induces. It is also used in combination with iron oxide and lampblack. Its colour is bluish-black and its specific gravity 6·396.

Bone Black.—Black pigments are usually produced by burning various materials, generally waste products. Bone black is thus obtained from bones, lamp black from oil, vegetable black from coke and scrap wood and gas, or carbon black, from natural gas. (Confined, of course, to America.) Ivory black, to be genuine, should be prepared from ivory chips, but bone black is the material usually sold for this variety. The blacks are stable and resistant to acids and alkalies.

Bone black, the ground product of bones which have been burned at a high temperature for several hours, contains a large proportion of calcium phosphate as well as carbon. It is generally a good inhibitor and is a satisfactory substitute for lamp black and carbon black in many cases.

Carbon black is a very pure form of carbon obtained by burning natural gas. It is often used in conjunction with white lead, but since it is known to be a stimulator, this practice is not advisable in the case of priming coats for iron and steel material. It may, however, be used with advantage in subsequent excluding coats.

Lamp black is again a pure carbon and is obtained by burning oils. Like carbon black, it is a conductor, and as such, unsuited for incorporation in priming coats. It appears to have a preservative action on the oil and is very stable and has pronounced colouring power. For purposes other than priming coats on iron, it is a very useful pigment.

Willow charcoal is made by charring certain kinds of wood. It has good inhibitive qualities, due, presumably, to the small quantities of alkali which it contains.

Calcium Carbonate.—There are two forms of this pigment, the natural form, whiting or chalk, and the artificially prepared form. The latter form is lighter than the natural variety, requires more oil for grinding, and often contains impurities which render its use inadvisable in protective paints. In small quantities it is advantageous, since it neutralises any free acidity in the paint, but large quantities are objectionable, since saponification of the oil is likely to occur and result in "chalkiness" and the destruction of the paint film. Mixed alone with oil, its "body" is very poor.

Calcium Sulphate.—This material is the hydrated sulphate of lime or gypsum and is usually prepared by pulverising the naturally occurring mineral and treating it so as to improve the colour. The final product is an excellent white and is much used in the compounding of various paints. It has little to recommend its use in protective paints, however; it is slightly soluble in water and its ionisation gives rise to acidity. These are serious objections, and its solubility gives it a tendency to wash out of the films.

China Clay.—China clay or kaolin is a natural aluminium silicate and finds considerable application as a substitute for barium sulphate in preparing certain pigments. It is a very permanent and fine white powder, and is often included in paints to arrest the sedimentation of heavier pigments.

Chrome Green.—This pigment was originally known also as Guignet's green and consists of chromium oxide. It is stable and permanent and finds much favour in railway work. It is an inhibitor, but its cost is a disadvantage. Ordinary chrome green is simply a mixture of chrome yellow and prussian blue, and various tones of colour, ranging from yellow to blue, are prepared, the blue from lead nitrate, sodium bichromate and sulphuric acid. The pigment so obtained is precipitated on to white lead and Chinese blue, and consists, therefore, of sulphate and chromate of lead, white lead, and Chinese blue. Its composite character may be looked upon as inferring impurity, and as nitrates of lead and soda may be present in addition, its inhibitive properties are problematic. The yellow-toned pigment is made in a similar manner, and the above remarks are applicable to it. Brunswick green consists of chrome green mixed with a large proportion of barytes.

Chrome Yellow.—Like chrome green, there are several varieties or tones of this pigment. The medium chrome yellow is the pure, neutral lead chromate, prepared by precipitating a lead salt with sodium chromate. Its inhibitive powers, which should be excellent, are generally unreliable since, during precipitation, it is so apt to carry down and include within itself various impurities. About eight different shades, ranging from orange to lemon, or canary, are manufactured. The orange shade is a mixture of the neutral and basic lead chromates, and is obtained by precipitating a lead salt with sodium chromate in the presence of an alkali. In spite of the many impurities which it may contain, it is generally a good inhibitor. Lemon chrome yellow is a mixture of the sulphate and chromate of lead, and is prepared similarly to the orange variety, except that the alkali used in the preparation of the latter is replaced by sulphuric acid and the bichromate of soda is used instead of the chromate. The method of its preparation, *i.e.*, the likelihood of the occlusion of acid in the precipitated pigment, precludes its inclusion amongst the inhibitive pigments, unless tested.

Graphite. Two forms of this material are used in the preparation of paints, the natural and the artificial forms. The latter is the purer and contains about 90 per cent. of carbon. They are valuable materials but have also certain objectionable features; as a conducting material, graphite is not suitable for use in priming coats, and it has such exceptional spreading properties that its application is not easy, and it is therefore usually incorporated with other heavy pigments to avoid the production of excessively thin films. For subsequent coats, however, graphite confers great durability on the paint, it is inert and has little or no action on the oil. Those varieties of natural graphite which contain relatively large amounts of silica appear to be the best as regards the durability given to the paint film. Such paints are very good water-shedders.

Indian Red. Venetian Red.—Indian red is usually prepared artificially from copperas or ferrous sulphate, though certain hæmatite ores are sufficiently pure and of good colour to be used. The best artificial varieties contain 95 to 96 per cent. of ferric oxide, and good hæmatites, when ground and levigated, yield an equally pure product. Many varying shades of Indian red are obtainable by modifying the process of manufacture, and the pigments are used alone or mixed with white lead or barytes. They are successfully used in inhibitive paints. Venetian reds were also originally made from iron ores, but they are now prepared by heating ferrous sulphate and lime, and consist, therefore, of calcium sulphate and ferric oxide. As already pointed out, calcium sulphate is liable to cause the production of acidity, and this pigment is not, in consequence, a good one to use in direct contact with iron. Other varieties, which are simple mixtures of ferric oxide and calcium carbonate, are safer from a corrosive point of view because of their freedom from acidity.

Iron oxide, itself, is used as a pigment and is made by roasting the sulphate of iron. It should not be used in priming coats unless it has been tested for traces of sulphate.

Litharge.—This is a heavy pigment, varying in colour from yellow to red, and is obtained by strongly heating lead in air. It is used very extensively and is, when pure, a very good inhibitor.

Lithopone.—Lithopone consists approximately of 70 per cent. barium sulphate and 30 per cent. of zinc sulphide, and is prepared by mixing together solutions of zinc sulphate and barium sulphide, when the compound pigment is precipitated. The precipitate is filtered and strongly heated and dropped, whilst hot, into water in order to disintegrate it. After washing, it is collected by filtration, dried, and reground. It is very permanent and stable and intensely white, but has a tendency to darken on exposure, though this fault often corrects itself. It is a fairly good inhibitor, but is not very well suited for exterior work unless mixed with other pigments such as zinc or calcium carbonate. It is much used, also, in the manufacture of high-class enamels.

Mineral Black.—This is chiefly used as an inert filler for paints, and is prepared by grinding certain varieties of slate. It contains as a rule large percentages of alumina and carbon, calcium carbonate, and iron salts, the principal constituent being silica. As a pigment it has little use.

Ochre. Sienna. Umber.—These pigments are all essentially oxides of iron. They vary considerably in composition and properties, and are not often used alone in paints for iron and steel. Ochre is chiefly used to tint white pigments and so produce varying buffs and creams. Sienna finds much favour in graining, and umber is of value for its characteristic purplish hue of rich brown. Vandyke brown is an allied pigment, richer and redder than umber, and much of it is made artificially from ochre, red oxide, and black. The ochres and umbers are very durable and are unaffected by admixture with other pigments.

Orange Mineral.—This has the same composition as red lead and is made by oxidising white lead. Its inhibitive properties are unreliable owing to the variations in its impurities.

Prussian Blue.—Prussian blue is made from ferrous sulphate and potassium ferricyanide and is a ferri-ferrocyanide of iron. The precipitate which is obtained by mixing the solutions of the two raw materials is oxidised. The pigment may contain traces of soluble salts, and its inhibiting qualities can only be ascertained by testing for purity. Some grades are good inhibitors, whilst others are stimulators. It has a preservative action on the oil, and paints compounded with it retain their gloss after long exposure. Chinese blue is a superior quality of Prussian blue.

Red Lead.—Red lead has been used in protective paints for many years, and is considered one of the best and most valuable pigments for this purpose. It is manufactured by oxidising litharge, either in furnaces or by heating the litharge with sodium nitrate. Its colour varies according to the mode of its production, as does also its inhibitive qualities. When pure, these are excellent, but when impurities are present, these may be greatly reduced. It is advisable, therefore, to test the pigment if it is to be used in priming coats for iron work. When mixed with oil, no other driers are necessary, since the red lead itself is an extremely rapid drier. Sulphurous atmospheres discolour it, turning it brown. It is very heavy, specific gravity 8·86, and admixture with other materials is a common practice to overcome this objection.

Ultramarine Blue.—This is a bright blue pigment prepared by calcining silica, China clay, sulphur and soda-ash and then grinding the product. Its sulphur content prevents it from being a good inhibitor and also causes it to darken when applied to iron, due to the formation of ferrous sulphide. It is mixed with zinc oxide to secure various tints and is permanent, except in the presence of alkalies, and it cannot be used in conjunction with white lead.

White Lead.—White lead is, perhaps, the most important of the white pigments. Its composition may vary slightly but may be considered to be $2PbCO_3 + Pb(OH)_2$, that is, basic lead carbonate. There are several processes of manufacture, the oldest being the Dutch or "stack" process. This process required about two months to produce the material, whilst the more recent "Quick" process requires only two weeks. Dilute acid is used in each process, and as a result the products are unreliable from an inhibitive point of view. The Dutch method consists in subjecting lead plates or grids to the action of dilute acetic acid and carbon dioxide, which latter is produced, together with the requisite temperature, by the fermentation of tan bark with which the pots containing the lead and acid are covered. The product is collected from the residual lead, ground in water, and dried. The Quick process is identical in essentials, but is speeded up by acting on finely divided lead with dilute acetic acid and carbon dioxide, the latter produced from coke or limestone. The process is conducted in revolving cylinders. A third process, the "Mild" process, consists in suspending finely divided lead in water through which air is blown. Lead hydrate is produced and is then carbonated. No acid is used in this method of manufacture, and the product is therefore unimpaired in its inhibitiveness. White lead is readily blackened by sulphurous fumes, and its akaline nature gives the paint a strong tendency to "chalk." It is adversely susceptible to atmospheric carbon dioxide and saline solutions, and is not used alone, therefore, but in conjunction with other pigments which tend to offset these objections, such as zinc oxide, etc. Sublimed white lead is produced by volatilising galena and is a basic sulphate of lead. It is a stable and fine pigment and is not blackened by sulphurous gases, and is fairly inhibitive.

Zinc Barium Chromate.—This pigment is prepared by precipitating a mixed solution of the chlorides of zinc and barium with sodium chromate It is a very good inhibitor and less soluble than the zinc salt alone.

Zinc Chromate.—The preparation of this yellow pigment is similar to that of the zinc barium chromate, except, of course, that the barium salt is omitted. It is also prepared from zinc oxide, potassium bichromate, and sulphuric acid. When free from acid, it is a good inhibitor, although usually containing other chromates and impurities. It is somewhat soluble in water and is costly. It is very valuable, even in small amounts, however, in protective paints.

Zinc Yellow.—This is a combined chromate and hydrate of zinc. It is a useful and non-poisonous pigment possessing good "body," is unaffected by sulphurous gases, and is without action on other pigments with which it may be mixed.

Zinc Lead White.—This is another compound pigment consisting of equal proportions of zinc oxide and lead sulphate. It is a sublimate produced by roasting sulphurous lead and zinc ores, the fumes being collected in fabric bags. It is often mixed with white lead and zinc oxide, is very stable, and generally has good inhibitive properties. The use and manufacture of this pigment appear to be restricted to the United States.

Zinc Oxide.—Zinc oxide is made either by burning zinc or by roasting zinc ores. In each case the product is collected in bags and is a sublimate. The pigment is very white and fine, and is non-poisonous and can be used together with any other pigment. That produced from metallic zinc is the purer. It is opaque and has good spreading properties. For use in white paints it is usually mixed with basic lead carbonate, and in this way serves two purposes, increases the spreading quality of the lead pigment, and reduces the hardness to which the paint film would dry if it contained zinc oxide alone. It is also a good inhibitor.

The following materials, though classed as pigments, are used for purposes other than tinctorial. They have little or no "body" themselves when ground in oil, but the addition of properly controlled proportions of them in a paint confers distinct advantages.

Barytes.
Barium carbonate.
Siliceous material.
Calcium carbonate.
China clay and like materials.
Asbestine.
Calcium sulphate.
Charcoal.

CHAPTER XIV

FEED-WATER TREATMENT

IF the earlier type of boiler is contrasted with the present-day type, we have the following comparison of working conditions: —

Old Type.	*Modern Type.*
Low pressure.	High pressure.
Low temperature.	High temperature.
Low rate of evaporation.	High rate of evaporation.
Low rate of concentration of soluble salts in the boiler.	High rate of concentration of soluble salts in the boiler.

As a result, the production of scale and the seriousness of corrosion were insignificant as compared with the rate of the development of these troubles and their progress in modern plants. Scale-forming impurities in the feed were precipitated more slowly and the temperatures and pressures prevalent were insufficient to render the potential corrosivity of certain salts actually kinetic. A modern boiler evaporates approximately one-half of its contents per hour, that is to say, in this period the concentration of soluble salts in the boiler water is increased by 50 per cent. and in one thousand hours the concentration would be five hundred times that in the feed. If the feed contains much raw make-up, an unworkable concentration may very soon be reached. A concentration of 1000 grains per gallon is generally regarded as the maximum permissible, and in no case is it considered good practice to exceed a concentration of 2000 grains per gallon.

Advances made in the more efficient and economical generation of steam have been accompanied, therefore, by increased risks of the development of very serious troubles, which, as previously pointed out, are not confined to the boiler alone, and if these advances are to remain truly economical and efficient and are not to be offset by greatly increased maintenance and replacement and cleaning charges, etc., it follows that they must be backed up by the production of non-scaling and non-corrosive boiler feed-water. After all, the efficiency of a plant is ultimately reduced to terms of £. s. d., and the treatment of boiler feed-water constitutes, therefore, a very urgent problem; one which has a direct bearing on the conservation of fuel and material and in which, fortunately, much progress has been made during recent years.

With the exception of the electrolytic methods of preventing the corrosion in boilers and condensers, which are based on an appreciation of the results of the contact of dissimilar metals or of the actual electrolytic mechanism of corrosion, all processes of feed-water treatment have for their object the elimination of the scale-forming and corrosive constituents in the feed, be it raw water, condensed water, or, as is more usual, a mixture of both. Softening processes are designed to remove the temporary hardness by actually removing the scale-forming impurities and to remove the permanent hardness by replacing the corrosive salts by non-, or less corrosive salts. The temporary hardness is that due principally to the bicarbonates of lime and magnesia, and is, therefore, a measure of the scale-forming character of the water. The permanent hardness, on the other hand, is that due to such salts as the nitrates, sulphates, and chlorides of lime and magnesia (and to salts of iron and aluminium, etc.), and is an indication of the corrosive character of the feed, with the exception, of course, of the sulphate of lime.

Degassing or deactivating processes are directed towards the removal of the dissolved gases oxygen and carbon dioxide in the feed-water, the complete treatment of which should include, therefore, both a softening and a degassing process. It is, of course, obvious that in the case of plants in which the major portion of the feed is condensed steam, the softening process need only be required to deal with the make-up water, but the removal of the dissolved gases in existing plants generally entails the treatment of the whole volume of the feed, since the condensate, whilst free from saline impurities and uncontaminated with raw make-up, has so many opportunities of dissolving atmospheric gases at various points in the circulation system, such, for instance, as in open hot wells and by its turbulent discharge into them, and by aëration in the pumps owing to imperfectly sealed glands, etc. In addition, the condensate very frequently contains a large quantity of dissolved gas, irrespective of any subsequent aëration. The proceeding applies to plants equipped with surface condensers. In the case of boilers fed from jet condenser discharge, it may be necessary to soften the whole of the feed.

SOFTENING PROCESSES

The Chemistry of Water Softening. The chemistry of softening is perhaps the simplest aspect of the whole problem, involving but the simple precipitation of the salts conferring temporary hardness and the simple interchange of radicles between the corrosive soluble impurities, or permanent hardness, and the chemicals employed in the softening process. A non-scale-forming and non-corrosive, or substantially less corrosive, water is thus produced. Sodium carbonate and lime are the chemicals most commonly used in softening plants, and they operate in the following manner, the lime dealing with the temporary hardness and the sodium carbonate with the permanent hardness :—

$$(18)\qquad \underset{\text{soluble}}{\overset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2}} + \overset{\text{Lime}}{Ca(OH)_2} = \underset{\text{insoluble}}{\overset{\text{Calcium carbonate}}{2CaCO_3}} + \overset{\text{Water}}{2H_2O}$$

$$(19)\qquad \underset{\text{soluble}}{\overset{\text{Magnesium bicarbonate}}{Mg(HCO_3)_2}} + \underset{\text{insoluble}}{\overset{\text{Lime}}{Ca(OH)_2}} = \underset{\text{insoluble}}{\overset{\text{Magnesium and Calcium carbonates}}{MgCO_3 + CaCO_3}} + \overset{\text{Water}}{2H_2O}$$

The addition of lime will thus remove or precipitate the temporary hardness by decomposing the soluble bicarbonates of lime and magnesia, and the precipitated carbonates may then be removed either by filtration or settling or by a combination of these processes. The carbonate of magnesium is still sensibly soluble in water, and for this reason it is necessary to add more lime than would appear to be called for by equation (49). If this extra quantity of lime is provided, the following reaction occurs :—

$$\begin{array}{lllllllll} & \text{Magnesium carbonate} & + & \text{Lime} & = & \text{Magnesium hydrate} & + & \text{Calcium carbonate} \\ (50) & MgCO_3 & + & Ca(OH)_2 & = & Mg(OH)_2 & + & CaCO_3 \\ & \text{slightly soluble} & & & & \text{insoluble} & & \text{insoluble} \end{array}$$

The magnesium hydrate is, practically speaking, insoluble. Hence the quantity of lime required to deal with magnesium bicarbonate is double that required to deal with an equivalent quantity of calcium bicarbonate. The magnesium hydrate is very light, and the precipitate settles much less readily than the calcium carbonate precipitate, and magnesium carbonate is therefore looked upon as more difficult to remove than the corresponding lime salt, and when a softening plant has been erected and put into operation by the makers troubles often occur when their experienced supervision is removed and the plant is left to the care of the customers, and of these troubles those due to the incomplete elimination of magnesium salt are amongst the most common The admission of the finely divided magnesium hydrate into the boilers or its formation therein is, as we have already seen, a source of priming and allied troubles.

The removal of the permanent hardness may be illustrated by the following equations :—

$$\begin{array}{lllllllll} & \text{Calcium salts} & + & \text{Sodium carbonate} & = & \text{Sodium salts} & + & \text{Calcium carbonate} \\ & CaSO_4 & + & Na_2CO_3 & = & Na_2SO_4 & + & CaCO_3 \\ (51) & Ca(NO_3)_2 & + & Na_2CO_3 & = & 2NaNO_3 & + & CaCO_3 \\ & CaCl_2 & + & Na_2CO_3 & = & 2NaCl & + & CaCO_3 \\ & \text{soluble} & & & & & & \text{insoluble} \end{array}$$

The reactions in the case of magnesium salts are similar, but since it is necessary to decompose the magnesium carbonate which would be produced as above, the sodium carbonate must be supplemented by the calculated quantity of lime, and the reactions which ensue result, not in the simple transformation of the magnesium salt into the carbonate, but proceed farther to form the hydrate :—

$$\begin{array}{lllllllllll} & \text{Magnesium} & + & \text{Sodium} & & & = & \text{Sodium} & + & \text{Calcium} & + & \text{Magnesium} \\ & \text{salts} & & \text{carbonate} & + & \text{Lime} & & \text{salts} & & \text{carbonate} & & \text{hydrate} \\ (52) & MgSO_4 & + & Na_2CO_3 & + & Ca(OH)_2 & = & Na_2SO_4 & + & CaCO_3 & + & Mg(OH)_2 \\ & Mg(NO_3)_2 & + & Na_2CO_3 & + & Ca(OH)_2 & = & 2NaNO_3 & + & CaCO_3 & + & Mg(OH)_2 \\ & MgCl_2 & + & Na_2CO_3 & + & Ca(OH)_2 & = & 2NaCl & + & CaCO_3 & + & Mg(OH)_2 \\ & \text{soluble} & & & & & & & & \text{insoluble} & & \text{insoluble} \end{array}$$

Since a properly operated softening plant prevents scale formation by actually removing the responsible constituents from the water, it is not uncommon nor surprising to find that the treatment of the permanent hardness is also regarded as a removal of saline impurities, and that, in consequence, the frequency and extent of blowing down, as a means of keeping the saline concentration of the boiler water within reasonable limits, may be considerably cut down. As a matter of fact, it is clear from the above that the treatment of permanent hardness does not involve a removal of salts, but rather a substitution of salts, and the concentration of saline matter in the water is thereby actually increased. In the case of magnesium sulphate, for instance, the equivalents of this salt and sodium sulphate, by which it is replaced, are :—

$MgSO_4$	Na_2SO_4
120	142

so that in removing 120 grains of magnesium sulphate from the water, 142 grains of sodium sulphate are substituted for it, an increase of 22 grains or approximately 18 per cent. on the original saline concentration due to magnesium sulphate. In the case of calcium sulphate, which would ultimately be wholly precipitated in the boiler, its removal with sodium carbonate represents a nett addition of 142 grains of dissolved solids for every 136 grains of sulphate of lime removed.

Softening by means of lime and sodium carbonate is the procedure which is generally adopted. The reagents are relatively cheap, and the control of the process, as represented by the quantities of these required, is simple. There is, however, another method available in which the use of caustic soda may wholly or partially replace the above reagents. In the first place it decomposes the bicarbonates, producing the normal and insoluble carbonate of lime and the hydrate of magnesia, equation (53). Secondly, the sodium carbonate, produced in the first series of reactions, proceeds to destroy the permanent hardness, as shown in equation (51).

	Bicarbonates	+ Caustic soda		Calcium carbonate	Magnesium hydrate	+ Sodium carbonate	+ Water
(53)	$Ca(HCO_3)_2$	+ $2NaOH$	=	$CaCO_3$		+ Na_2CO_3	+ $2H_2O$
	$Mg(HCO_3)_2$	+ $4NaOH$	=		$Mg(OH)_2$	+ $2Na_2CO_3$	+ $2H_2O$
	soluble			insoluble	insoluble		

It will be seen that unless the permanent and temporary hardness are exactly equivalent, this method will either result in an excess of caustic soda or of sodium carbonate in the treated water. If the destruction of the temporary hardness produces insufficient sodium carbonate to deal with the permanent hardness and the amount of caustic soda added is calculated on the temporary hardness, the water will be imperfectly softened. If, on the other hand, the caustic soda is calculated on the total hardness and the temporary hardness is less than half of the total, an excess of caustic soda will remain in the water. If, again, the permanent hardness is small in comparison to the temporary hardness, then an excess of sodium carbonate will go forward in the treated water. Neither an excess of sodium carbonate nor of caustic soda is desirable when originating in this way, and this process is only suitable, therefore, in those very exceptional cases where the nitrates, chlorides, and sulphates of lime or magnesia are exactly equivalent to the temporary hardness. It is not a standard process, and, moreover, it is relatively expensive and is more difficult to control than the lime-soda process.

In certain cases, in which the permanent hardness is due largely or solely to sulphate of lime, it is possible to remove this impurity in such a manner that the concentration of soluble salts in the treated water is reduced by the amount represented by the calcium sulphate. It will be remembered that the treatment for permanent hardness made with carbonate of soda results in a conversion of the soluble salts of lime and magnesia into the less harmful sodium salts, but that the concentration of saline matter in the treated water was actually increased. If, however, a barium compound is included in the lime-soda treatment, it is possible to eliminate the sulphate of lime without adding to the water an equivalent quantity of some other soluble salt. Instead of an equivalent amount of sodium sulphate, an equivalent amount of the insoluble barium sulphate is produced which may, of course, be eliminated together with the other precipitated material. When calcium sulphate is present in large amounts and represents the major portion of the total impurity, this process is of undoubted value, and although it is expensive, it would probably be more economical in the long run in cases such as the ones just indicated than the standard process.

The removal of sodium carbonate and of iron and aluminium salts from natural waters in which these impurities occur in abnormally large amounts necessitates the use of additional reagents in the softening processes. Sodium carbonate is destroyed either by alum (aluminium sulphate) or by calcium chloride. In the latter case the reaction is simple, and results in the precipitation of calcium carbonate and the substitution of sodium chloride for the sodium carbonate:

$$(51)\quad Na_2CO_3 + CaCl_2 = CaCO_3 + 2NaCl$$

If alum is used, the sodium carbonate is replaced by sodium sulphate and aluminium carbonate is produced. This compound, the result of the combination of a weak acid with a weak base, cannot exist as such, and immediately splits up into free carbon dioxide and insoluble hydrated alumina:

$$(55)\quad \begin{array}{l} Al_2(SO_4)_3 + 3Na_2CO_3 = 3Na_2SO_4 + Al_2(CO_3)_3 \\ Al_2(CO_3)_3 + 3H_2O = 2Al(OH)_3 + 3CO_2 \end{array}$$

It will readily be seen that each of these treatments requires very careful control. If calcium chloride is used, serious trouble may be anticipated in the boilers if the quantity employed is in excess of that required to deal with the sodium carbonate. The same may be said of alum. An excess of this reagent will, like the calcium chloride, pass the filters in a soluble form and be pumped into the boilers, where it will dissociate into hydrated alumina and an equivalent quantity of free sulphuric acid. The former may cause priming and the latter will certainly cause corrosion. Moreover, the evolution of carbon dioxide in the softener (equation 55), as a result of the reaction between the sodium carbonate and the alum, requires the addition of an extra calculated quantity of free lime, lest this gas should also be admitted to the boilers. When properly controlled, however, either process is satisfactory, and if, as should be the case, the chemicals are proportioned so as to leave a little residual carbonate alkalinity in the treated water, there can be no danger of the calcium chloride or of the alum getting into the boilers.

The removal of iron and aluminium salts is effected by means of lime or sodium carbonate. If iron is present in sufficient quantity to necessitate its removal, it is usually in the form of the corrosive ferrous sulphate. Treatment with lime or sodium carbonate results in the formation of ferrous hydroxide or carbonate, both of which are, on oxidation, precipitated as ferric hydroxide. The reaction whereby aluminium salts are removed by sodium carbonate is identical with that already given to illustrate the removal of sodium carbonate with alum. In fact, but for a reversal of objective, the processes are exactly alike. In this case, however, it is advisable to use a slight excess of the softening reagent, carbonate of soda, whereas in the previous case it is equally, and for the same reasons, advisable to have a slightly insufficient amount of the softening reagent, alum.

The Calculation of Quantities.—The units used in this country in connection with boiler feed-water and its impurities are the grain and the gallon. Thus the results of an analysis of a water express the amounts of the impurities as so many grains per gallon. The quantities of reagents used in softening plants are calculated in terms of pounds per thousand gallons of water. Now as one gallon weighs ten pounds and one pound contains 7000 grains, it is a simple matter to express the amount of, say, calcium carbonate, as pounds per thousand gallons. If, for instance, the analysis records the amount of this impurity as 5 grains per gallon, the amount in 1000 gallons equals $5 \times 1000 \div 7000$ pounds, that is $5 \times \frac{1}{7}$ pounds. Grains per gallon $\times \frac{1}{7}$ equals, therefore, pounds per thousand gallons. Knowing the quantity of impurity in these terms, the amount of softening reagent required to deal with it is then readily calculated from the chemical equivalents. Take calcium sulphate, for example, which is removed by means of sodium carbonate:—

$$(56) \quad \underset{136}{CaSO_4} + \underset{106}{Na_2CO_3} = CaCO_3 + Na_2SO_4$$

One hundred and thirty-six grains of sulphate of lime require 106 grains of sodium carbonate to completely precipitate them. One grain will therefore require $\frac{106}{136}$ grains of sodium carbonate and one thousand gallons of water will require $\frac{106}{136} \times 1000$ grains of sodium carbonate for each grain of calcium sulphate per gallon, that is $\frac{106}{136} \times 1000 \div 7000$ pounds of sodium carbonate, equals 0·1113 pound. This figure, 0·1113, is the factor for calcium sulphate. It assumes, of course, that the sodium carbonate is 100 per cent. pure, and if this is not the case it must be increased in proportion to the reduced percentage of soda ash contained in the reagent.

Calcium carbonate is held in solution by free or semi-combined carbon dioxide, and its removal by lime may be effected by calculating the quantity of this reagent on a free carbon dioxide basis, since the removal of this gas is essential to the precipitation of the carbonate of lime.

$$\underset{44}{CO_2} + \underset{74}{Ca(OH)_2} = CaCO_3 + H_2O \tag{57}$$

As before, 44 grains of free carbon dioxide require 74 grains of lime, or, one grain will require $\frac{74}{44}$, or 1·682 grains of lime. One thousand gallons of water will thus require $1{\cdot}682 \times 1000 \div 7000$ or $1{\cdot}682 \times \frac{1}{7}$ pounds of lime for each grain per gallon of carbon dioxide, that is 0·240 pound. This figure is the factor for free carbon dioxide, again assuming the lime to be 100 per cent. pure. Considerable variation in the actual $Ca(OH)_2$ content of successive consignments of lime is inevitable, and the factor must therefore receive suitable correction based on the purity of the reagent, and it may be conveniently emphasised here that the control of softening plants should always be extended to include frequent analyses of the reagents employed. In fact, it is impossible to control the process if this is not done, and neglect in this direction frequently follows immediately on the customer taking over the operation of the plant from the contractors.

The factors for other impurities in natural or other waters may be obtained in a similar manner to the above illustrations, but it must not be forgotten that the necessary quantities of reagents thus found are theoretical, and that it is often necessary either to exceed this figure somewhat and leave an excess of the reagent in the treated water, or to reduce it in order to avoid the possibility of an excess of the reagent in the treated water. These modifications will be determined by the characteristic features of the case in point, but having a readily obtained basic or theoretical figure, it is easy to increase or reduce it by a predetermined amount. It is always necessary to provide, for instance, an excess of sodium carbonate in order that the reactions shall proceed to completeness, and to ensure a slight alkalinity of the treated water.

Boiler Compounds.—It is still a fairly common practice to introduce into the boilers a chemical or a solution of chemicals with a view to preventing the corrosion and the formation of scale. All reactions between the boiler fluid and the boiler water impurities will, as a result of this procedure, take place in the boilers, and this fact alone goes far towards discounting any advantages which might appear to lie in the ease of application of boiler fluids. With certain exceptions, the use of these compounds instead of a softening plant cannot be recommended, particularly with regard to large plants. Their use may be likened to the administration of an emetic after deliberately allowing poison to be consumed, and the more intelligent procedure is obviously to prevent the consumption of the poison or, in other words, to treat the water before it enters the boiler. The boiler is designed to raise steam and not to purify its feed-water. Often no treatment at all is preferable to the use of boiler compounds of which some may be compounded from waste products, are apparently intended to be universally applicable, and have no regard for the specific requirements of the client's particular water. Even assuming that a boiler fluid does cause the scale-forming constituents of the water to be precipitated as sludge, the resultant condition of the water may be such as to cause violent priming and to necessitate frequent and wastefully excessive blowing-down. Further, where the compound or fluid is of unknown composition, and it is not always that this is advertised, there is the risk that it may develop or produce acidity or corrosive products in the boiler. Whilst some boiler fluids are undoubtedly compounded scientifically and to suit the requirements of each customer's water, there are others which are fancy-priced and useless if not actually dangerous.

One material, the use of which as an anti-corrosive boiler compound, would appear to be justified, is potassium dichromate. Even this, however, is dangerous if the water contains much sodium chloride, since the reactions between the salt and the dichromate will produce free hydrochloric acid, and although the chromium salts may have a protective action on the boiler, this acid will manifest its presence in other units of the plant.

It may be that in certain cases the character of the water is such that it can be successfully treated by the use of a boiler fluid of known and predetermined composition and which is used in the correct proportions.

These cases are confined almost entirely to small plants such as in laundries, small vertical boilers, etc., and the like, and the fluid must be compounded from a consideration of the characteristics of the water in question and the quantity used per unit period of time must be properly controlled. There can be no such thing as a universally applicable boiler fluid or compound, and if a boiler water requires treatment, especially in large steam-raising plants, it is more satisfactory, and, in the long run more economical, to effect this in a properly designed and controlled softening plant.

SOFTENING PLANTS

The choice of a softening plant should not be unduly influenced by a consideration of initial outlay, and it is also a matter which calls for expert advice. A badly designed plant may introduce a greater proportion of troubles than was experienced prior to its installation, but a properly designed and controlled softener may be relied upon to operate efficiently and automatically, for long periods, with a minimum of attention and repairs. Softeners consist essentially of (1) gear for handling the softening reagents and mixing them, (2) gear for correctly apportioning the reagents to the quantity of water, and (3) a large settling tank at the bottom of which the eliminated scale-forming impurities collect. The mixing and apportioning, or proportioning, gears are generally operated by the incoming water, and a filter is also usually incorporated in the plant itself, though it is the custom to instal additional filters as separate units.

The chief desiderata of a softening plant may be considered under the following headings :—

(1) Size.
(2) Operation.
(3) Settling capacity.
(4) Construction.

The size of the plant should be designed to conform to the maximum working speed, that is to say, the apportioning gear, reaction tanks, and settling tanks must be dimensioned from this basis. The water should take at least two hours to pass through the reaction and settling chambers, and the capacity of these in a plant dealing with 1000 gallons per hour should therefore be at least 2000 gallons, and the more the better. In passing through the settling tanks, the direction of the flow of the water should be upwards, since the settlement of precipitated matter is facilitated in this way; if the treated water left the settling tanks via the bottom there would be a very considerable risk of it carrying sediment with it. The plant should operate continuously and automatically. The power may be obtained from the incoming water, and the mechanism whereby this power is utilised should be arranged so that the possibilities of its ceasing to operate through the development of mechanical troubles are reduced to a minimum. This power should also be employed to continuously agitate the softening reagents; the lime, for instance, settles very rapidly in the reagent or chemical tank, and unless its agitation is thoroughly effective the softening will not be uniform.

The apportioning gear should be sufficiently robust to operate for long periods with but little or no attention or adjustment, etc., and it should also operate normally under all conditions of the reagent tank, *i.e.* whether this be full or almost empty. If the gear is of the tipping bucket type, it must be sufficiently sensitive or well balanced to tip with precisely the same volume of water at all times. Hence, all bearings and moving parts should be well protected against dirt and corrosion and should be fitted with reliable lubricating arrangements. The gear should also work equally satisfactorily much below its rated capacity. In special cases, where it is necessary to use alum as a coagulant in order to ensure efficient filtration, the apportioning gear must be made of material which will withstand the corrosive action of this chemical. Thus wooden or lead-lined tanks and vulcanite gear may be necessary.

The chemical tanks should be large enough to avoid more frequent recharging than necessary, and this operation should, of course, be possible while the plant is in action. The arrangements for handling the supplies of reagents should be simple and convenient, and in many cases it is desirable to provide these on the ground level, a small hand pump being fitted to raise the mixed reagents to the chemical tank on the top of the softener. The gear provided for sludging the settling tanks must be accessible and effective. In certain types of plant, in which the reactions and settling take place in the same tank, it is desirable not to keep the bottom of this entirely free from mud or sediment, since the presence of a small quantity hastens the precipitation of the lime and magnesia from the incoming water by causing the formation of larger particles. At the same time, however, undue accumulations of sediment should not be permitted, and in plants where reaction and settling take place in separate compartments, it is the best practice to keep the settling tank as clean as possible.

Effective filtration of the softened water is ensured in modern plants by the provision of separate filters in addition to the one which is integral with the softener. The satisfactory operation of these is governed by general principles of industrial filtration, and need scarcely be considered here beyond some remark as to cleaning. This is usually effected by mechanical stirring or by agitation with compressed air

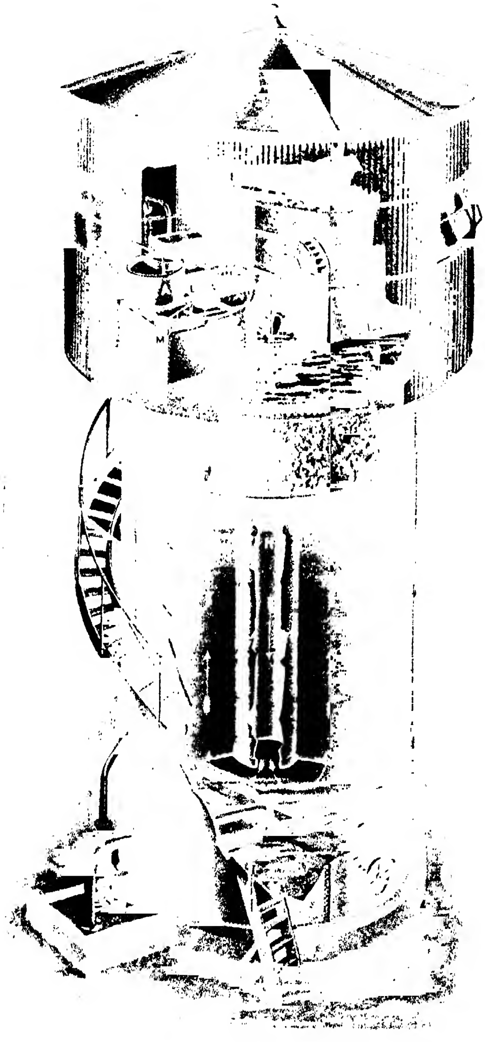

FIG. 17.—KENNICOTT CYLINDRICAL TYPE SOFTENER.

and is an essential operation in the proper control of the softening plant; one which should be carried out thoroughly and at regular intervals.

Finally, all moving portions of the plant should be readily accessible for inspection, adjustment, etc., and the platform accommodation should therefore be substantial and ample.

The modes of operation of softening plants may be best described by considering those of some of the most up-to-date plants. Fig. 17 gives an excellent idea of the construction of one of the Kennicott Co.'s machines. The top portion houses the reagent tanks, apportioning gear, etc. Immediately below this is placed the filter, then comes the reaction and settling tank, and, at the bottom, the sludging gear. The calculated quantities of softening chemicals required for the day's operation are charged into the tank, B, which is filled to a definite level. The raw water enters by the pipe, E, into the box, F, from which it flows, through an adjustable slot, over the water-wheel, D, and out of the chute, G, at the bottom of the water-wheel casing, into the top of the downtake, H. The raw water provides all the power necessary to operate the plant by passing over the water-wheel. It drives the main horizontal shaft to which the water-wheel is keyed, and the two vertical shafts in the chemical tank and downtake respectively are driven off the main shaft by bevel gears. The

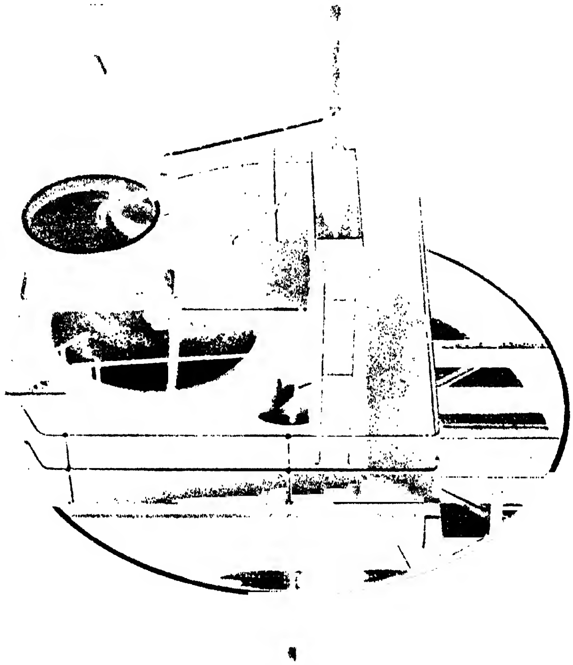

FIG. 18.—KENNICOTT APPORTIONING GEAR.

shaft in the chemical tank is fitted with a four-bladed agitator at the bottom, and this keeps the chemicals constantly and thoroughly mixed. The shaft in the downtake has a number of agitators fitted to it, and this ensures that the chemicals added are thoroughly mixed with the water.

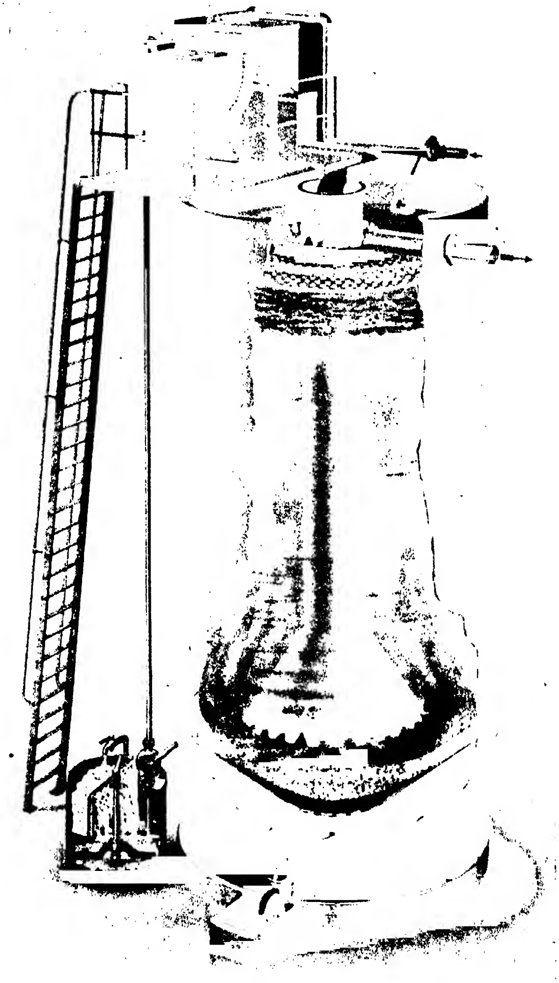

Fig. 19.—Paterson Cylindrical Type Softener.

In order to proportion the chemicals, a small quantity of the raw water is by-passed into the dividing box, I, where, by means of an adjustable slide, an exact proportion is delivered to the regulating tank, K. The slide is set so that the quantity of water delivered to the regulating tank fills it in a definite number of hours. In the regulating tank is a float attached over pulleys to a weir in the chemical tank, and, as the regulating tank fills, therefore, the weir in the chemical tank is lowered at exactly the same rate and the chemicals which overflow the weir are delivered into the top of the downtake with the hard water. It will thus be seen that the quantity of chemicals added is in exact proportion to the quantity of raw water entering the plant. Immediately the chemicals come into contact with the water, the whole is thoroughly mixed by mechanical agitation in the downtake.

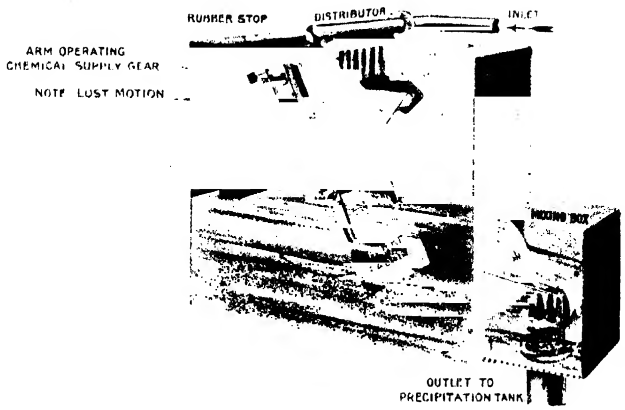
RUBBER STOP
DISTRIBUTOR
INLET
ARM OPERATING CHEMICAL SUPPLY GEAR
NOTE LOST MOTION
MIXING BOX
OUTLET TO PRECIPITATION TANK

FIG. 20.—PATERSON "OSILAMETER" MEASURING BUCKET.

The water, having had the correct quantities of chemicals added and mixed with it, flows down the downtake to the bottom of the settling tank, and, taking the direction shown by the arrows, flows upwards at a very slow rate and is finally filtered at the top of the plant. The hardening salts are precipitated and the bulk of the precipitated matter settles to the bottom of the tank, whence it is removed at regular intervals by means of the revolving sludging gear. The last traces of the precipitated matter are removed by the filter. Fig. 18 gives a closer view of the apportioning gear of the Kennicott softener.

Fig. 19 shows a sectioned perspective view of a Paterson softener. In general principle it is similar to the one described above, differing mainly in the design of the apportioning gear, which is shown in detail in figs. 20, 21, and 22. The raw-water measuring device comprises a twin compartment oscillating receiver or "Osilameter," mounted on suitable bearings, fig. 20. Each compartment is so

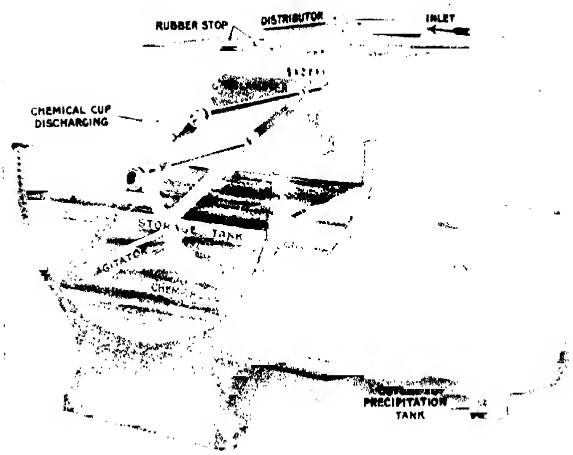
RUBBER STOP
DISTRIBUTOR
INLET
CHEMICAL CUP DISCHARGING
STORAGE TANK
AGITATOR
PRECIPITATION TANK

FIG. 21.—PATERSON "OSILAMETER" AND CHEMICAL TANK.

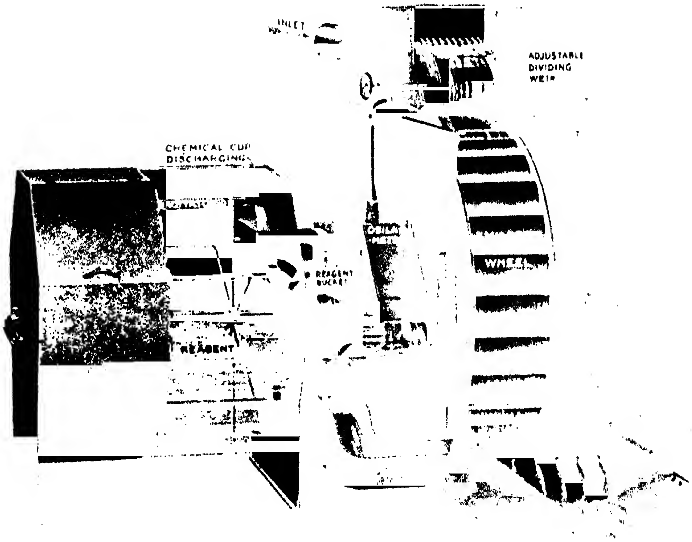
INLET
ADJUSTABLE DIVIDING WEIR
CHEMICAL CUP DISCHARGING
REAGENT BUCKET
REAGENT
WHEEL

FIG. 22.—COMPLETE PATERSON APPORTIONING GEAR WITH WATER WHEEL AS FITTED TO LARGER UNITS.

arranged that after a definite volume of water has entered it, a small surplus overflows into a lip at the outer extremity. The first slight tilting movement of the "Osilameter" instantly floods this extension lip, producing a powerful leverage which overturns the receiver, discharges the contents, and brings the adjacent compartment into the filling position. A brake paddle absorbs the momentum of the "Osilameter" as it falls towards the fixed stops, and it is also free to fall the first 15 degrees before any auxiliary gear is engaged; thus there is no initial drag on the bucket until it has acquired sufficient momentum to overcome all frictional resistance in the moving parts.

Fig. 21 shows the chemical tank *in situ* relative to the "osilameter." The reagents are added by chemical cups holding a definite quantity and operated by the swing of the oscillating bucket. By this means the proportioning is automatically controlled for all rates of supply of the raw water. The contents of the chemical tank are agitated by paddles operated by the "osilameter" in smaller plants, or by a water-driven power wheel in the larger sizes, fig. 22. As each measured quantity of water is discharged by the "osilameter," the requisite amount of softening reagents is added by either of the chemical cups and thoroughly incorporated by the turbulent motion of the water in the mixing and averaging box.

The arrangement supplied on large plants is shown in fig. 22. The raw water enters the weir chamber and, after passing through a baffle plate to remove the surge, overflows a weir having an adjustable partition which bye-passes a definite proportion of the total flow through the "osilameter." This discharges the precise weight of chemicals required for satisfactory treatment of the whole supply. The main flow of the incoming water operates a water wheel which drives agitating paddles in the chemical tank. Cups attached to these paddles keep the reagent measuring bucket continually charged, the surplus overflowing back to the chemical tank. The fall of the "osilameter" overturns the reagent measuring bucket, and both water and reagent are discharged into the mixing chute, the empty compartments of each vessel assuming the filling position. The bye-passed water containing the chemicals is thoroughly mixed with the bulk supply in the baffled mixing trough into which the water wheel discharges.

After leaving the measuring and mixing gear, the water enters the central drop pipe, fig. 19, and gradually descends to near the base of the reaction tank, where, owing to the large sectional area, it becomes almost quiescent. The impurities settle to the bottom and the water passes slowly upwards, reaching the wood fibre filter practically free from suspended matter. The capacity of the reaction tank depends upon the nature of the water treated, and may range from one and a half to six times the maximum hourly output. The sludge is collected in smaller plants by a conical hopper-shaped bottom and in larger plants by a rotating scraper into the central sump and discharged periodically. The lime and soda mixture is prepared in a hand- or power-driven mixing mill on the ground level and the contents are raised to the chemical tank by a pump or steam jet elevator. The power-driven type of mixer is fitted with rollers to grind the line into a smooth and homogeneous paste.

The Lassen-Hjort cylindrical type of water softener is shown in fig. 23, whilst fig. 24 depicts the measuring and mixing gear. The water to be softened is conveyed by a pipe which alternately fills each of the compartments of a two-chambered tipper mounted on a shaft. When one of these compartments is full of water, the tipper overbalances and discharges its contents into the tank in which it is mounted

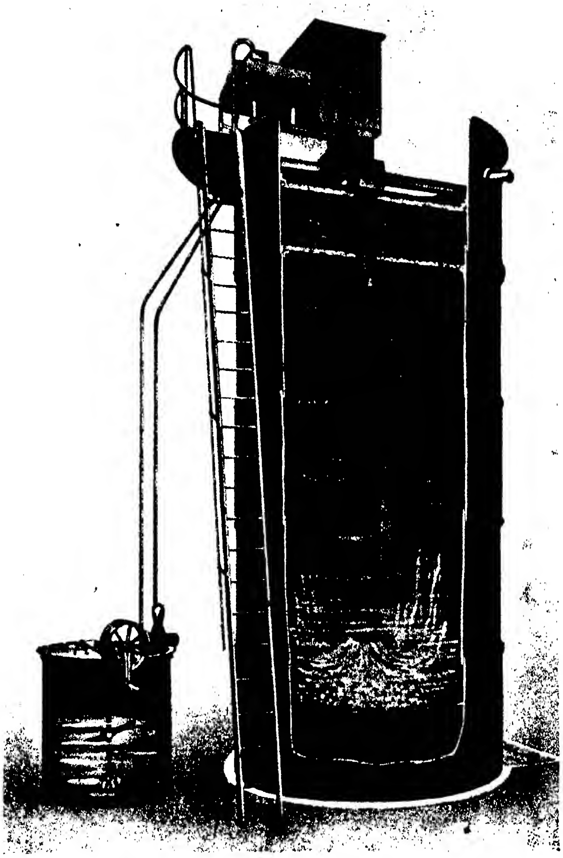

FIG. 23.—LASSEN-HJORT CYLINDRICAL TYPE SOFTENER.

and, at the same time, the empty compartment is brought into the filling position and receives the raw water from the inlet pipe. A definite quantity of raw water is thus measured out at each oscillation, and, as this is discharged from the tipper into the tank, a corresponding amount of water is displaced from this tank through a standpipe into the reaction chamber, where it receives at the same moment the requisite charge of chemical solution from the chemical container fixed at the side of the tipper tank. This apportioning of chemicals is effected by means of a "Positive Discharge Valve" placed in the bottom of the chemical container, which is opened at each movement of the tipper, delivering the exact quantity of softening reagents into the reaction chamber. The valve can be adjusted to discharge any specified quantity of reagent required by the volume of water in the upper compartment. It can therefore be regulated to meet variations in the amount of impurities in the raw water without changing the solution of chemicals in the chemical tank. This valve constitutes an essential feature of the Lassen-Hjort softener. Details of it are shown in fig. 25. It consists of a fixed cylinder, A, riveted to the bottom of the chemical reservoir, and into which screws an adjustable cylinder, B, fixed in any desired position by the back-nut, C. Within these cylinders work two valves, D and E, the latter screwing on to a tail-piece, F, projecting from the valve D. The pitch of the threads on this tail-piece and on the adjustable cylinder being the same, any movement of the cylinder, B, results in a corresponding movement of the valve E, which has a feather, G, working in a key-way, H, cut into the cylinder, B. It will be seen that the valve D is provided with a flat face and a piston body, and this latter prevents any chemical solution being admitted into the adjustable cylinder until the lower valve, E, has closed the outlet ports, J. The operating gear consists of a double lever, K, fixed to the rocking shaft, L, of the tipper. These levers are fixed to the vertical valve spindle by two loose links, M, and trunnions, N, clamped

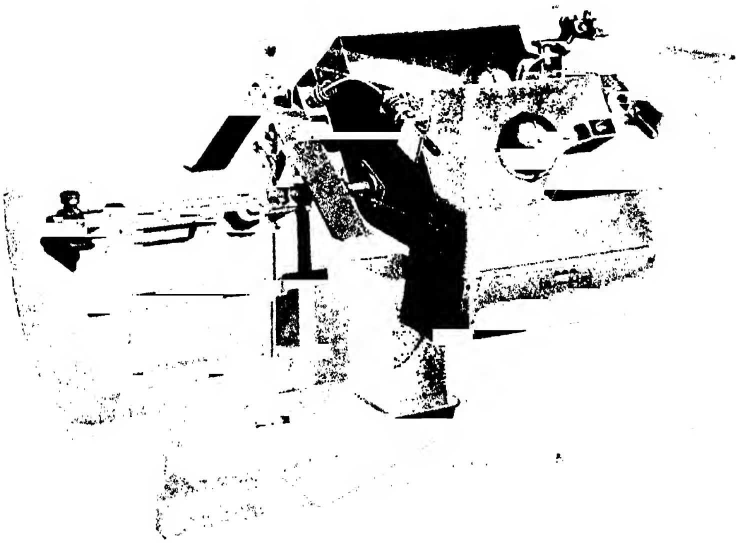

Fig. 24.—Lassen-Hjort Measuring and Mixing Gear.

against a screwed sleeve, O, by the lock nut, P. When in operation, these levers impart an up-and-down motion to the valve. The screwed sleeve, O, works between rollers, Q, carried on the bridge, R, and the weight, S, keeps the valve, D, tight on its seat.

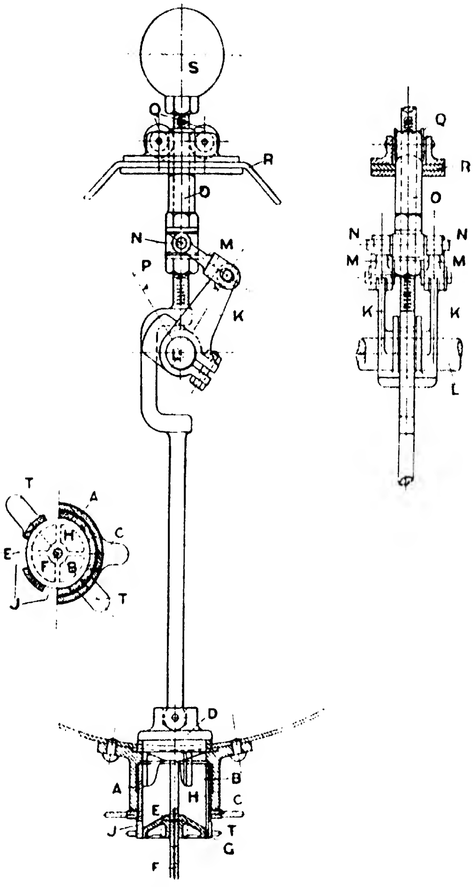

Fig. 25.—Lassen-Hjort "Positive Discharge Valve."

Another feature of the Lassen-Hjort plant is a locking arrangement, operated by floats, which prevents any accidental tipping of the measuring buckets until they have filled to the prescribed limit.

The softening plants so far described are all of the cold-process, cylindrical type. In certain cases, for instance where head room is restricted, or for other reasons, a horizontal type may be installed. The proportioning gear remains unaltered, but the actual removal of precipitated matter is effected in two compartments. In the first of these, the reaction between the softening reagents and the impurities in the raw water proceeds and the bulk of the sediment is deposited. The flow of the water is upwards through a filter and then over a weir into the bottom of the second chamber and again upwards through a second filter. Figs. 26 and 27 illustrate two types of horizontal softeners.

Hot-Process Softeners.—In the hot-process softeners, waste steam from auxiliaries etc., is made use of to accelerate the reactions between the raw water impurities

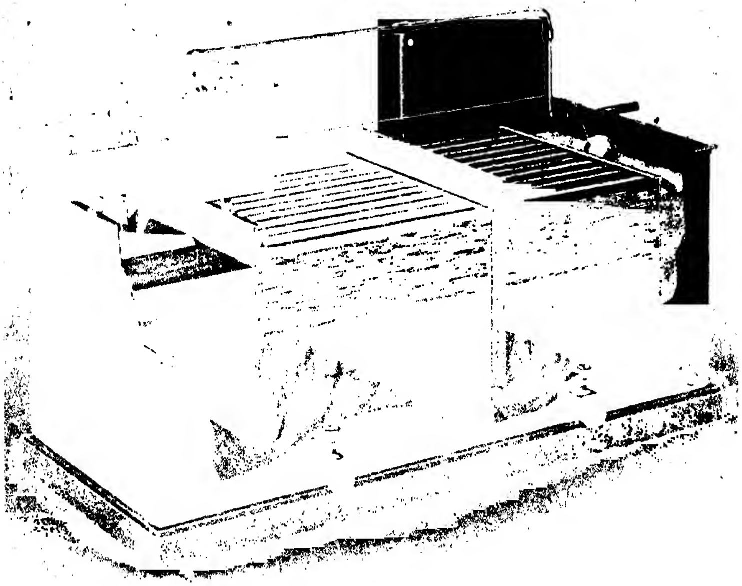

FIG. 26.—LASSEN-HJORT HORIZONTAL TYPE SOFTENER.

and the softening reagents, and also, at the same time, to raise the temperature of the boiler-feed so that separate feed-heaters may be dispensed with. The general arrangement of a hot-process softener is the same as that of the cold-process plants, except that there is included a chamber in which the exhaust steam and raw water meet, the temperature of the latter being raised to a degree determined by the proportion of steam available. In other Heater-Softeners, the raw water is heated by flowing over trays in an iron chest, the exhaust steam passing upwards through the cascade of water. If sufficient steam is available, the water is raised to the boiling point, and any carbonate of lime present is precipitated on the trays, but if magnesium salts are also present, lime is necessary to convert them into the insoluble form of hydrate. Any permanent hardness must also be dealt with by sodium carbonate. As pointed out, however, chemical softening is accelerated by heat.

The Kestner Continuous Blow-Down is perhaps the most recent refinement of hot-process softening. When a boiler is fed with water which has been softened in the usual way, the soluble salts in the treated water become concentrated in the boiler. If the softening has been correctly carried out, the character of the water will be slightly alkaline, but there will always be, in addition, a minimum of about 0·05 grain of calcium carbonate per litre, and if the boiler water is allowed to exceed a certain concentration the carbonate of lime will commence to precipitate and will produce a scale which is hard because of its slow rate of deposition. Generally, this is avoided by periodical blowing-down which, in the ordinary way, entails the loss of a considerable amount of heat. The Kestner Continouus Blow-Down system is designed to conserve this heat and to remove the salts in the boiler water before the depositing concentration is reached, and the blow-down itself is used to assist in the chemical reactions which take place in the softener proper. In softening by means of soda, a slight alkalinity of the treated water is always an objective, and it is this trace which, after concentration in the boilers, of course, is utilised in the further softening process. The blow-down, containing sodium carbonate, is discharged into a purifier, where it mixes with and raises the temperature of the make-up, and, in cooling, deposits a large proportion of its calcium carbonate content. The tempera-

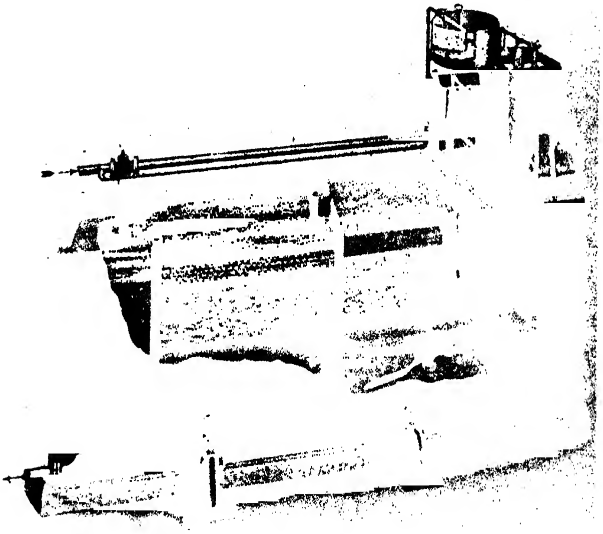

Fig. 27.—Paterson Horizontal Type Softener.

ture of the make-up water is raised to about 100° C. by the blow-down, and at this temperature the sodium carbonate reacts with the bicarbonate of lime in the make-up and precipitates it as the normal and insoluble carbonate, and, at the same time, any sulphate of lime is removed by conversion to sodium sulphate. Owing to the high temperature, these reactions are more complete and proceed more rapidly, the precipitates produced are larger in grain size, and therefore settle more quickly, aided, in addition, by the reduced viscosity of the water, which at 100° C. is only 25 per cent. of the viscosity at 15° C.

In the boiler, the bicarbonate of soda, already partly decomposed in the purifier, is converted into the neutral carbonate and, on leaving with the blow-down, is used again in the purifier, and it corresponds exactly to that which served previously to precipitate the carbonate of lime. Since the percentage blow-down is regulated so that its sodium carbonate content is sufficient to precipitate the calcium carbonate in the make-up, it is never necessary to adjust this quantity of soda once the plant has been started up and balanced. It is necessary only to adjust the amount of soda required to deal with the sulphate of lime and other impurities.

The Kestner purifying system includes also apparatus for degassing (see section on same), and as the purification just described is performed at an elevated temperature, an appreciable quantity of dissolved gas in the make-up is removed in consequence, and this considerably lightens the load on the degassers. The amount of reagent is adjusted so that the water leaves the purifier or softener with a slight alkalinity, and this, in conjunction with the subsequent action of the degassing plant, results in a water of which the corrosive tendencies are reduced to a minimum and from which the deposition of scale is impossible.

Fig. 28 shows, diagrammatically, the rectangular type of purifying vessel. In common with other softeners, it consists essentially of three portions, the measuring gear, the reaction chamber, and the settling chamber. The operation is automatically controlled by the quantity of treated water leaving the apparatus. The delivery of the make-up water is controlled by a ball float valve, 1, so arranged that the quantity of make-up entering is dependent upon the quantity of feed-water leaving the softener. The reagent is run from the soda tank, 14, into the reaction chamber, control over its quantity being obtained by a rocking mechanism, 6, which is actuated by the make-up water. The reagent is in this way mixed automatically with the make-up in the required proportions and no attention other than that involved in the replenishment of the soda tank from the dissolving tank, 13, is necessary. A counter, 11, fitted to the rocking mechanism, serves to check the consumption of the reagent. The lower part of the rectangular tank forms the reaction chamber into which the mixture of raw water and reagent is fed. The boiler blow-down enters through an ejecto-condenser, 18, and is controlled by a ball float valve, 17, which regulates the delivery from the boilers as the demand on the purifier varies. The ejecto-condenser condenses the steam and causes the mixing, circulation, and agitation of the blow-down with the make-up water and soda. The settling tank is arranged in the lower part of the tank and is provided with vanes, 27, along its length which guide the dissolved gases, expelled in the process, to the vent pipe, 28. Before

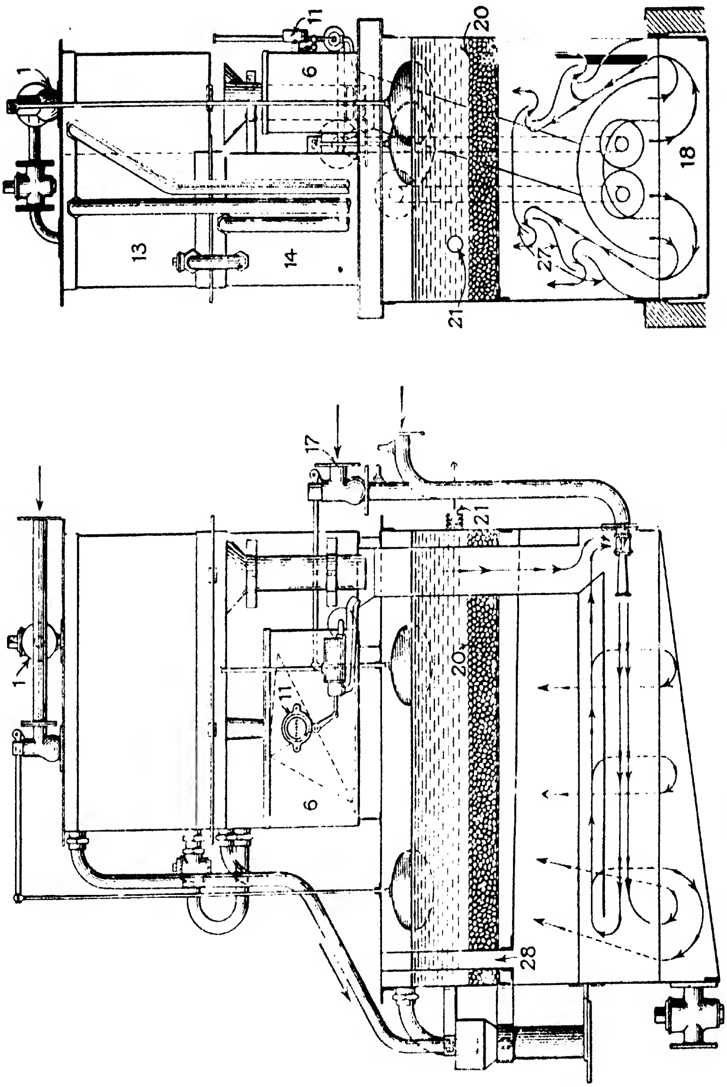
1
11
6
13
14
20
21
27
18
1
17
21
20
11
6
28

Fig. 28.—Kestner Softener as Used in Conjunction with the Kestner Continuous Blow-down System.

leaving the purifier, the water passes through a filter, 20, and then leaves through the outlet, 21, hot and clean.

The Kestner system, including the degassing apparatus effects therefore :—

(1) Conservation of heat in the blow-down.

(2) Limitation to a predetermined figure of the concentration of soluble matter in the boiler-water.

(3) Economy in the softening reagents by softening the make-up with salts contained in the blow-down.

(4) The blow-down itself is purified and returned to the boiler.

(5) Removal of all scale-forming salts externally to the boiler.

(6) Prevention of corrosion due to dissolved gases.

Permutit.—Attention has previously been drawn to the fact that natural waters may, by passing through peculiarly constituted geological strata, exchange their lime and magnesium contents for an equivalent amount of sodium, and that in this way many waters which are naturally strongly alkaline have acquired this characteristic by percolating through a layer of zeolite. The discovery of processes for artificially preparing zeolites has made possible a softening process which is perhaps the most simple one we have. It is absolutely automatic and requires no apportioning gear or power or chemicals such as lime and soda, which have to be periodically replenished. This process of softening is known as the Permutit Process,* and it is especially important because it will produce a water of zero hardness.

Zeolites can be prepared artificially, and the synthesised material possesses the characteristic base-exchanging property to a much greater degree than do the natural zeolites. Large quantities are now manufactured and used for treating water, not only boiler-feed, but also water required for many industrial purposes. Their application has also been extended to other fields, such as the recovery of material from dilute solution, etc., in industrial effluents.

The zeolites are prepared by igniting China clay or other silicate of alumina and sand or quartz with alkali carbonates. The fused mass is extracted with water and the residual permutite left as a granular mass. The more porous this mass, the more active is the artificial zeolite or permutit. Several varieties are produced, differing in the nature of the exchangeable base.

The complete removal of lime and magnesium salts from raw water may be effected by filtration through a sodium permutit :—

$$(58)\quad Na_2O,Al_2O_3,2SiO_2 + CaSO_4 = CaO,Al_2O_3,2SiO_2 + Na_2SO_4$$

A calcium zeolite is formed and the lime and magnesium salts originally present in the water are replaced by equivalent amounts of the corresponding sodium salts. After a time the permutit becomes exhausted, that is, completely converted into calcium permutit, and must be re-activated by treatment with a concentrated solution of common salt, which causes the reverse of the above reaction to take place. This treatment with sodium permutit may be relied upon to reduce the hardness of the raw water to zero. The removal of sodium salts from water may be similarly effected by employing a filtering bed of a calcium permutit, the re-activating solution in this case being one of calcium chloride.

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* The United Water Softeners Ltd. (Lassen Hjort).

The Permutit process is also available for the removal of iron and manganese from water. Starting with a calcium permutit, a manganese permutit is first prepared from it by treatment with a solution of manganese chloride :—

$$(59)\quad CaO,Al_2O_3,2SiO_2 + MnCl_2 = MnO,Al_2O_3,2SiO_2 + CaCl_2$$

The second stage of the pre-treatment consists in treating the manganese permutit with calcium permanganate. Manganese heptoxide is thereby precipitated throughout the mass of the material :—

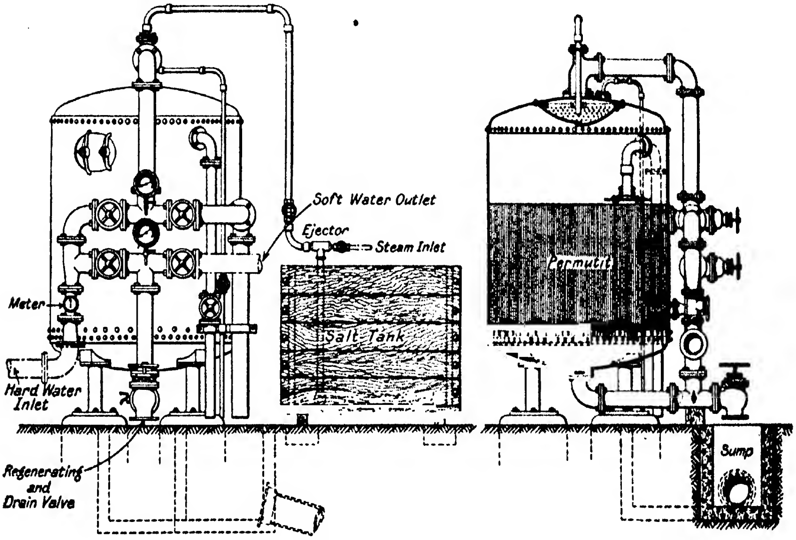

FIG. 29.—PERMUTIT SOFTENING PLANT.

$$(60)\quad MnO,Al_2O_3,2SiO_2 + Ca(MnO_4)_2 = CaO,Al_2O_3,2SiO_2 + MnO,Mn_2O_7$$

and it is this compound, rather than the permutit itself, which effects the removal of iron and manganese from the raw water. Its oxidising action precipitates these impurities as MnO_2 and Fe_2O_3,xH_2O respectively :—

$$(61)\quad 2Mn(HCO_3)_2 + MnO,Mn_2O_7 = 5MnO_2 + 2H_2O + 4CO_2$$

The manganese heptoxide, when exhausted—that is, when completely reduced by having oxidised the iron or manganese in the water—is regenerated by means of a solution of calcium permanganate. In removing iron, the action is supposed to be catalytic, the manganese heptoxide accelerating the oxidation of the iron salts by the dissolved oxygen present in the water. Whatever the actual mechanism of the process may be, it constitutes the most efficient method of removing iron from water that is available, excepting, of course, the use of evaporators.

The chief objection to Permutit softening as applied to the treatment of boiler-feed water, is that it replaces the hardness-producing salts by sodium salts, and if the hardness due to carbonate of lime is high, there is a risk of developing an excessive concentration of sodium carbonate in the boilers. This may be avoided by first reducing the carbonate hardness to 2 or 3 degrees by means of lime and then completing the process in a permutit plant. On the other hand, it offers a method of successfully treating waters rich in sodium carbonate. This salt can be converted into calcium carbonate by a calcium permutit, and then the water may be treated or softened with lime in the usual manner to remove that portion of the carbonate of lime retained in solution by any free carbon dioxide.

Fig. 29 shows the general design of the Permutit softener.

THE REMOVAL OF GREASE

Condensed water, whether from surface or jet condensers, is rarely free from oil or grease, and the use of such water for boiler-feed is not advisable, even though the water be otherwise satisfactory. The efficient elimination of oil and grease is therefore another problem added to the treatment of boiler-feed water. Grease cannot be completely removed from steam by mechanical means in which the steam is caused to impinge on baffle plates, etc., since even if it assumed that the heavier portions of the oil are thus removed, the volatile portions will obviously remain in the steam. The removal of grease from condensed steam is more readily effected, but even in this case no simple process, such as ordinary filtration, will suffice. The oil is frequently in an emulsified state, imparting a "milkiness" to the water, and the size of the individual particles of oil is probably of the order of one ten-thousandth of a inch in diameter. Before this oil can be dealt with practically, it must be coagulated, that is, reduced to particles of larger size, capable of being retained by a filter. The coagulation process is the one now generally adopted by the leading softening contractors, and is the only reliable method of ensuring a satisfactory elimination of oil and grease from the boiler-feed. The coagulant used is aluminium sulphate, from which alumina, $Al_2(OH)_6$, is precipitated by means of soda-ash. This precipitate is of such a nature that it entangles all kinds of suspended matter, no matter how finely divided. When first produced, it is distributed evenly throughout the mass of the water as an invisible, jelly-like substance. Subsequently this contracts and breaks up into flakes, and these, which are easily filterable, retain all the finely divided oil and grease.

The aluminium sulphate may be precipitated by the temporary hardness salts in the water, and if these are present in sufficient quantity, the ordinary softening process may be readily arranged to include the de-oiling of the water as well; in fact, in some cases, the coagulant may be omitted, since the lime and magnesia precipitates, produced during the softening, may remove the oil without any additional assistance. Particularly does this apply to the magnesia precipitate. The alum is necessary, however, if the temporary hardness is insufficient to produce a large enough precipitate, and if the exhaust steam or condensate is treated separately, a second reagent, such as soda-ash, must be employed to precipitate the alumina from the aluminium sulphate.

Fig. 30 shows a combined softener and de-oiler of a type which is employed in cases where the make-up is sufficiently large in volume to necessitate its treatment in a softener, and where, at the same time, the condensate must be freed from oil and grease. The condensate and make-up are discharged into separate measuring and mixing apparatus, one of which adds the softening reagents to the make-up whilst the other adds the coagulant to the condensate to remove the oil from it. In treating the condensate, the chemical tank is divided into two compartments, one containing soda and the other the alum. The condensate and reagents meet in a chute, from whence they are discharged into a compartment where the coagulation takes place. Most of the alumina and entangled oil is thrown down as a sludge, and is removed via a sludge cock, whilst the provision of suitable filters ensures the removal of the last traces of coagulated oil. Where both jet and surface condensers

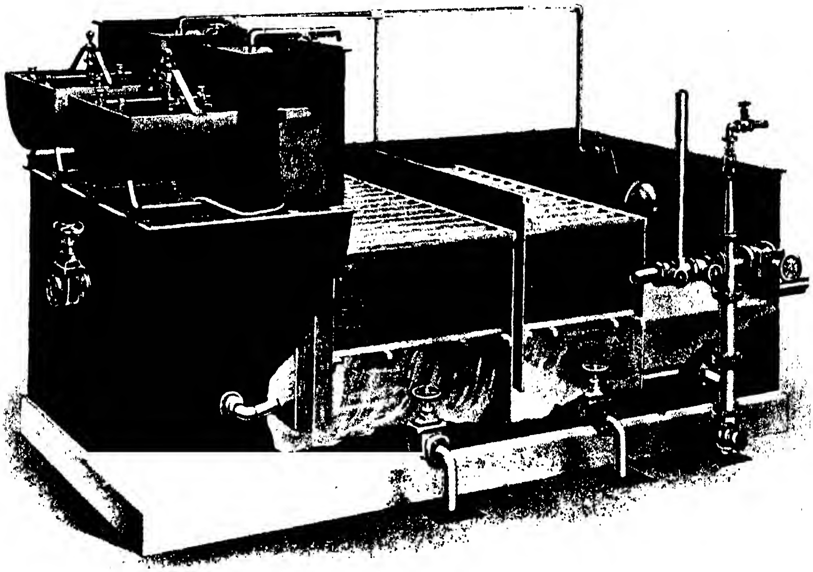

FIG. 30.—LASSEN-HJORT COMBINED SOFTENER AND DE-OILER.

are used, the make-up constitutes a large portion of the feed, and it is preferable in these cases to instal separate plants for softening and de-oiling.

Another typical oil eliminator is shown in fig. 31. The greasy condensate enters the measuring chamber and overflows through a rectangular or V notch. A float resting on the water in this weir chamber controls the position of two long tapered valves, giving anular orifices which discharge the reagents in accurate proportions to the amount overflowing the weir. The oily condensate and reagents are thoroughly mixed in a baffling trough before passing into the reaction and precipitating tank, where the bulk of the "coagulate" is arrested by filtering upwards through a wood-fibre filter, final purification being effected by downward filtration through quartz sand.

The proportion of the reagents used for eliminating oil should, of course, receive careful attention; if soda-ash is used to precipitate the alumina from the alum, it is obvious that an insufficiency of this, relative to the aluminium sulphate, will result in the admission of this corrosive agent into the boilers. It is desirable to emphasise this, since the alum is so superior a coagulant to lime or magnesium precipitates that its use is always preferable.

There is still another form of plant in which the oil may be removed by coagulation and in which the process is primarily electrical. A series of iron plates is arranged in parallel and close together, and the water to be de-oiled is made to flow between them. These plates serve as electrodes for an electric current, the result of the passage of which is to produce a precipitate of hydroxide of iron. This precipitate acts similarly to that obtained from the aluminium sulphate and entangles the finely divided oil and grease and carries them down with it. Combined sedimentation and filtration then removes the precipitated iron, and the oil held by it, from the water.

THE REMOVAL OF DISSOLVED GASES

Excluding industrial pollution which is responsible for the presence of "unnatural" atmospheric constituents such as sulphur trioxide, sulphur dioxide, sulphuretted hydrogen, etc., the two constituents of the atmosphere with which we are concerned are oxygen and carbon dioxide. It is now agreed that these gases, dissolved in boiler feed-water, may be responsible for very serious and rapid corrosion in the boilers, and particularly in the pipe-lines, economisers, and other units of a power plant. How far boiler corrosion is due to these gases, in the absence of corrosive salts, is, as already pointed out, not readily ascertained, particularly if the boilers are of a type in which the restriction of the circulation is a minimum. Few will dispute, however, their disastrous effects on the superheaters, turbines, etc., though there is still a diversity of opinion as to which of the two gases is the most responsible. The balance of opinion probably lies in favour of, or rather in disfavour of, oxygen. Carbon dioxide alone can, of course, attack iron, since its solution in water constitutes carbonic acid. Oxygen alone dissolved in water may or may not have any action on iron, according to whether the original electrolytic theory of corrosion is accepted or rejected. Its significance, however, lies in the fact that, even though

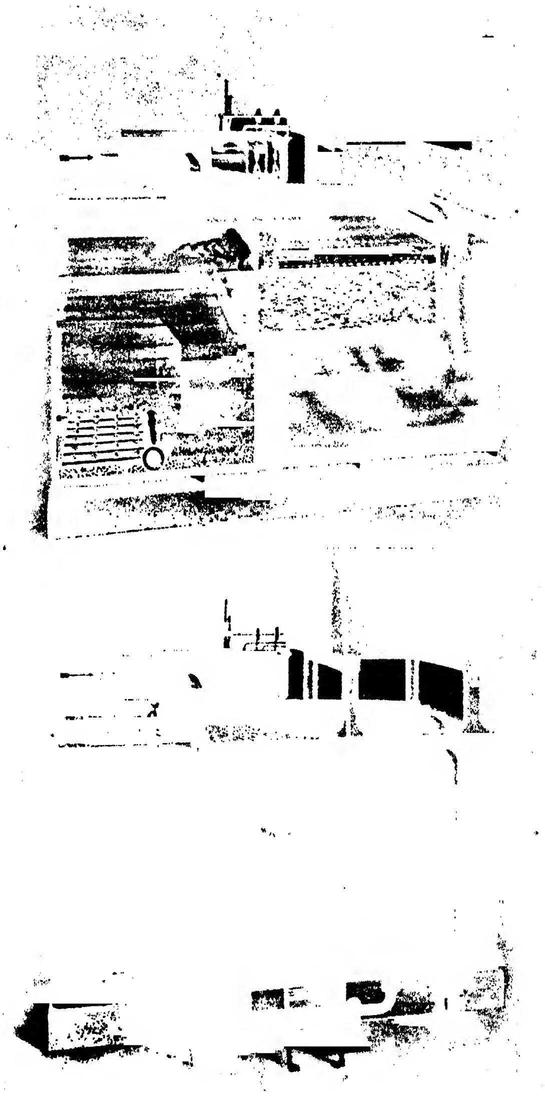

FIG. 31.—PATERSON COMBINED SOFTENER AND DE-OILER.

it be itself inert in this respect, there is always some other factor or influence present which renders it active. It never occurs in natural waters unaccompanied by carbon dioxide, and the effect of the latter is magnified many times by the oxygen. Again, even supposing a softening process removes with a hundred per cent. efficiency the free dissolved and semi-combined carbon dioxide, the presence of any previously formed products of corrosion in the plant will provide the necessary stimulus required by the oxygen to render the latter corrosive. There is little doubt that most corrosive influences may, in the absence of oxygen, become practically negligible. The nett result of corrosion is the wet oxidation of the iron or steel, and, with but few exceptions, all corrosive factors and water impurities assist the process mainly in its intermediate stages. Hence, the greater the amount of oxygen available, the more rapidly will the final product be formed, that is, the greater the amount of metal which will be corroded in unit time. Oxygen is corrosive in that it allows the corrosion or solution of the metal to proceed uninterruptedly by counteracting the natural forces which constitute reactions to solution pressure or corrosive action.

Softening processes may be arranged to eliminate scale-formation in the boilers and to replace the permanently soluble corrosive salts by less dangerous ones, but they do not normally provide any measure of protection to the superheaters, turbines etc., the corrosion of which may be excessive, even though the boiler-feed be perfectly softened water, and, in addition, composed of as much as 95 to 97 per cent. condensate. In such cases the corrosion can only be attributed to the dissolved atmospheric gases contained in the feed-water. The make-up, though a small proportion of the whole, is often almost saturated with dissolved oxygen, and if it is softened, the mixing and agitation in the softener tend to complete saturation or even to supersaturation. The oxygen content of the condensate (surface condensers being assumed) will vary with the peculiarities of the circulation system; turbulent discharge at any point, aëration in the pumps, and the evolution of gases from salts in the boiler, such as described by Paul in connection with the behaviour of sodium carbonate, all help to increase the dissolved oxygen content, and it is often the case that the condensate contains as much dissolved atmospheric gas per gallon as does the raw make-up.

It is now a well-established fact that corrosion can be prevented by eliminating dissolved oxygen from the boiler-feed. For practical purposes, the solubility of the mixture of gases, which forms the atmosphere, in water follows Henry's law, that is, the solubility is proportional to the pressure, and inversely proportional to the temperature. The relative proportions of oxygen and nitrogen dissolved are also proportional to their partial pressures in the atmosphere. Air consists of a mixture of eighty volumes of nitrogen and twenty volumes of oxygen, therefore their partial pressures are as 4 : 1. The solubility of nitrogen in water at N.T.P. is 18 cubic centimetres per litre and of oxygen 35 cubic centimetres per litre. Hence the quantities dissolved in water saturated with air at N.T.P. are :—

Oxygen :— $35 \times 0{\cdot}2 = 7{\cdot}00$ c.c. per litre.
Nitrogen :— $18 \times 0{\cdot}8 = 14{\cdot}40$,, ,,

Thus, whereas the atmosphere contains 20 per cent. of oxygen and a trace of carbon dioxide, the air dissolved in water contains about 33 per cent. of oxygen and a large amount of carbon dioxide. The carbon dioxide content of the air is normally about

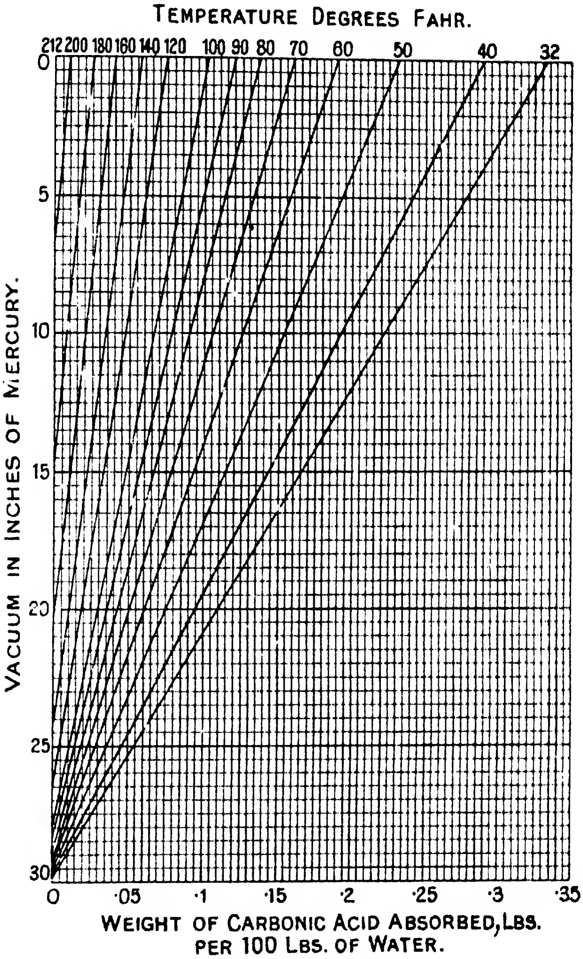

FIG. 32.—SOLUBILITY OF CO_2 IN WATER.

0·03 per cent. by volume, but its solubility in water is about thirty times that of oxygen, and is not, as in the latter case, controlled by its partial pressure, since it forms a compound with the water (carbonic acid) and is therefore "fixed" in a non-gaseous form. The quantities which may be dissolved in water under varying conditions of temperature from 32° to 212° F. and of pressure from 0 to atmospheric are shown in fig. 32. Fig. 33 shows similarly the amounts of oxygen which are absorbed by water under varying conditions of temperature and pressure.

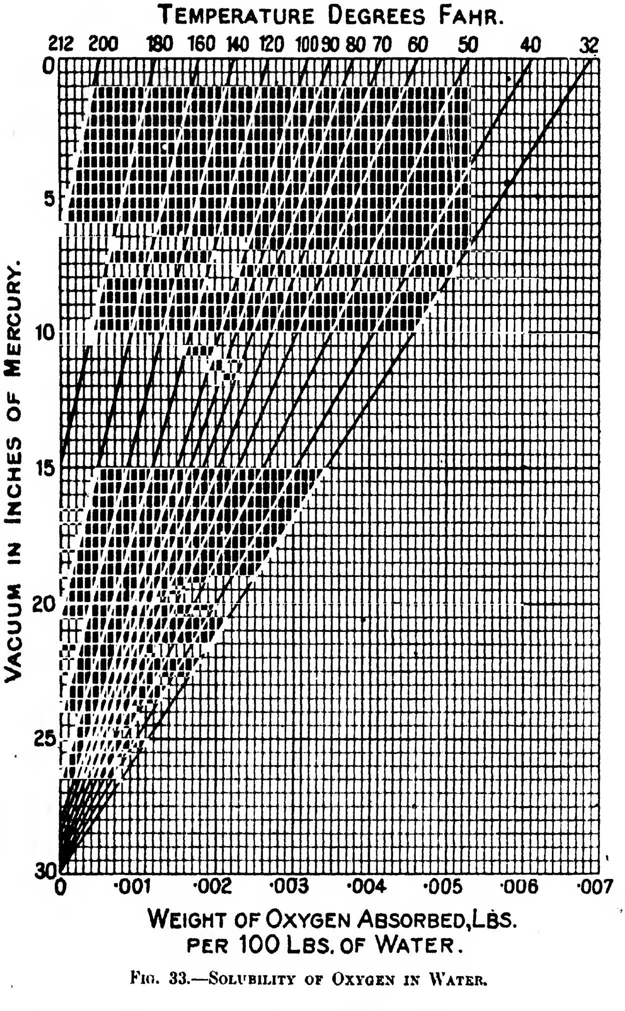

FIG. 33.—SOLUBILITY OF OXYGEN IN WATER.

The methods available for removing dissolved gases from water fall into two classes :—

(1) Chemical means.
(2) Physical means.

Chemical degassing, or, as it is sometimes called for purposes of distinction, "de-activating," consists essentially of an apparatus containing readily corrodible metal in the form of perforated sheets, turnings, or expanded metal, on which the aërated water may expend or exhaust its corrosive constituents before entering the boiler or circulation system. The Kestner degasser is typical of this type, fig. 34, and is designed to remove the residual oxygen left in the feed-water after this has been raised to the highest temperature possible in the plant of which the de-activator comprises a unit. It is not possible to remove the whole of the dissolved gases by boiling the water, and even the water extracted from the condenser under vacuum is not entirely freed from dissolved gas. The amount of gas is also often supplemented by aëration in the pump. The Kestner degasser removes these traces by chemical means. Referring to fig. 34, the water is deoxidised in the central portion of the vessel which is packed with finely divided steel, specially prepared both in respect to its chemical composition and physical condition, so as to be very readily corrodible. The apparatus is proportioned according to the quantity of water it has to deal with, and aims at the reduction of the oxygen content of the water to a limit at which the gas is insufficient in amount to be capable of injuring the metal of the boiler, pipelines, economisers, superheaters, etc. This limit represents an oxygen content of practically *nil*. The water inlets, 1 and 2, are so arranged on the vessel that the flow of water may take either an upward or downward direction, since, if the flow were always in one direction, the deoxidising material would, after a time, become coated with an impermeable film of oxide, which would seriously retard the process. By periodically reversing the flow of the water, the portions of the material which are most rapidly oxidised with, say, an upward flow, have a period of rest during which the film of oxide changes chemically into a form which is readily detachable and which does not interfere with the corrosion of the turnings when the direction of flow is again reversed. A steam injector, 6, causes insufficient agitation or turbulence to detach the oxide from the material, and the flow of water carries the oxide through the filters, 4, which detain it. The direction of flow is changed once every twenty-four hours, and the apparatus requires but little attention until the deoxidising material requires renewing.

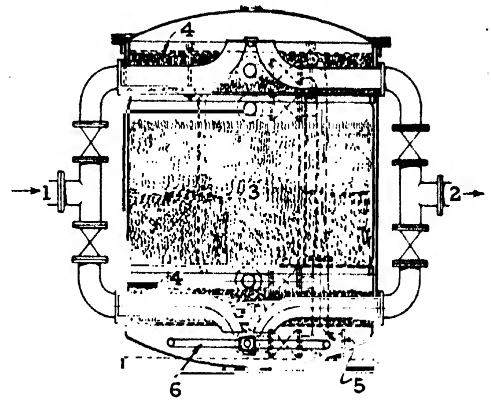

Fig. 34.—Sectional View of the Kestner Chemical Degasser.

The operation of this type of degasser is purely chemical, and consequently its efficiency is to a large extent determined by the temperature of the water entering. The higher this is, the more rapid is the chemical process whereby the oxygen is removed and therefore the smaller may be the size of the installation necessary to handle a given quantity of water. The apparatus is recommended for use in conjunction with the Continuous Blow-down already described, and the water produced by the Kestner system as a whole is free from dissolved gas, from scale-forming and corrosive salts, and contains a slight excess of alkalinity. This is in line with what is generally considered to be the best type of boiler-feed.

Fig. 35 gives a general idea of the appearance of the Kestner type of degasser. A degasser, somewhat similar to the Kestner apparatus, but using expanded sheet instead of turnings, has been investigated by the Metropolitan-Vickers Electrical Co., Ltd. (See the discussion to Kestner's paper, "The Degassing and Purification of Boiler Feed-Water," *Proc. Inst. Mech. Eng.*, June 1921.)

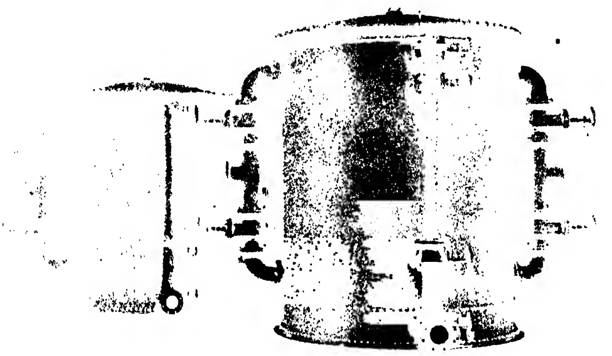

FIG. 35.—GENERAL APPEARANCE OF THE KESTNER CHEMICAL DEGASSER.

Other plants for chemically degassing water are those of Hulsmeyer, Seiffert, and Walker. They are alike in principle in that the corrosive constituents of the water are expended on cheap and readily replaceable metal instead of in the power plant units. Some of them combine also physical degassing in the process, but the arrangements for this are of a secondary nature. The only chemical method in use is the one described.

Physical methods of degassing are of three kinds, thermal, vacuum, and agitation, and they are often combined in the same apparatus. The agitation method alone is very imperfect, but it can be usefully employed to assist in the thermal and vacuum processes or in the combined thermal and vacuum processes, particularly if it is applied in such a manner that it breaks up the water into a spray. An increase in temperature lowers the solubility of the dissolved gases in water, but, starting from the cold, no gas is evolved until a temperature of about 75° C. is reached, and up to this point the water becomes increasingly supersaturated with oxygen, etc., in solution. Above 75° C., gas bubbles begin to form, and at the boiling point the dissolved gas is quickly given up until only about 2 cubic centimetres per litre remain. If the water is agitated, however, the elimination of gas is continuous from the commencement of heating, and the residual 2 cubic centimetres per litre, left in solution at the boiling point, may be still further reduced by continued boiling. The degassing action of the steam bubbles comes into play and the partial pressure of the oxygen in the air above the boiling water is reduced by the displacement of the air by the steam. Boiling can eliminate most of the dissolved gas in this way, but it must be prolonged.

The vacuum process removes the dissolved gas in a manner analogous to the effect of a steam atmosphere above the surface of the boiling water. Up to the boiling point the removal of the gas is effected by heat and is purely a thermal action, but the actions of a steam bubble, steam atmosphere, or a vacuum are quite of another kind. Since the quantity of gas dissolved by water is proportional to the partial pressure of the gas in the atmosphere above the liquid, it is clear that if the partial pressure of the gas in the supernatant atmosphere is reduced, then the solubility of the gas in the water will also be proportionately reduced. The water will give up gas to the atmosphere in an attempt to restore the natural equilibrium between the quantities of gas in the two media. In a vacuum or steam atmosphere the partial pressure of oxygen is practically *nil*, and if water containing this gas in solution is injected into a chamber in which is maintained a vacuum or steam atmosphere, it will give up its dissolved oxygen. The appreciation of the relation between the partial pressure of a gas and the quantity of it dissolved by water is the fundamental principle of all physical degassing processes. The degassing action of steam bubbles, which is not generally appreciated, may be explained in the same way; when a steam bubble is formed the partial pressure of oxygen in it is *nil*, and as a result the bubble proceeds to degas the water immediately in contact with it. In a boiler, where the formation of steam bubbles is extremely rapid, their degassing effect will be considerable and the steam generated will contain, as a result, by far the larger proportion of oxygen entering the boiler in solution in the feed-water, and it is for this reason that the effects of dissolved oxygen are often manifested so severely on subsequent units of the plant, and it may also give some support to the statement, made some few pages back, that it is difficult to ascertain how far the dissolved oxygen is directly responsible for corrosion in the boiler itself.

The most common method of de-aërating boiler feed-water is by simultaneously lowering the pressure and raising the temperature. A sectional view of an apparatus for effecting this is shown in fig. 36, which depicts the Weir Direct Contact Heater. The heater inlet is connected to the discharge of hot well pump, and comparatively cold feed-water at atmospheric pressure is drawn from the hot well and pumped into the heater through a spring-loaded spray valve. Heating steam, obtained from auxiliary exhaust or some other source, is led into the heater through the non-return valve, B, on the side of the apparatus. The cold feed-water is thus instantly heated by contact with this steam, and as the pressure in the heater is much less than that of the entering water the effect of the reduction in pressure and the sudden heating is to liberate the dissolved air from it. This air is removed to the condenser or atmosphere by way of the cock, K, on the air vessel placed on the top of the heater. The feed-water is in this way rendered non-corrosive and falls to the bottom of the heater at the boiling temperature corresponding to the pressure, and flows direct to the feed pump suction, whence it may be delivered to the boilers without further contact with the atmosphere.

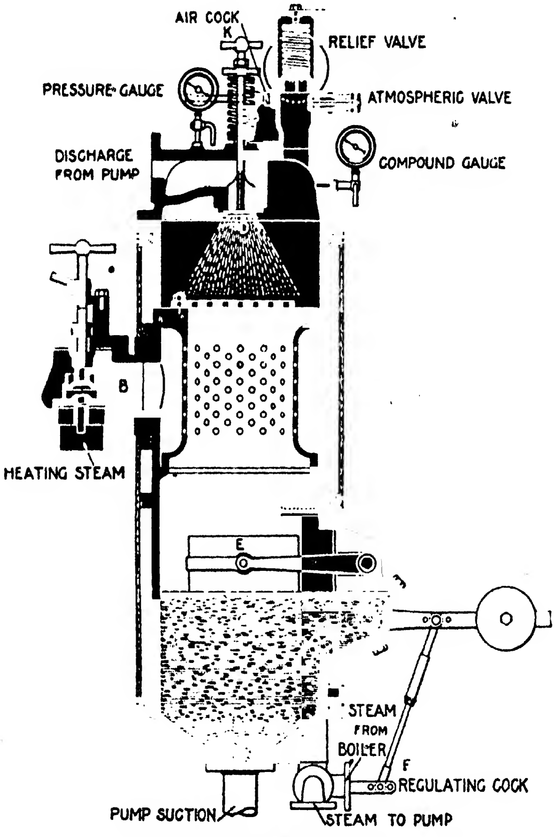
AIR COCK
K
RELIEF VALVE
PRESSURE GAUGE
ATMOSPHERIC VALVE
DISCHARGE FROM PUMP
COMPOUND GAUGE
B
HEATING STEAM
E
STEAM FROM BOILER
F
REGULATING COCK
PUMP SUCTION
STEAM TO PUMP

Fig. 36.—Weir Direct Contact Heater.

The Weir Direct Contact Heater may be readily installed in existing power stations. Assuming that the plant consists of several independent units, running on an open system, the usual arrangement will be that the water is pumped from

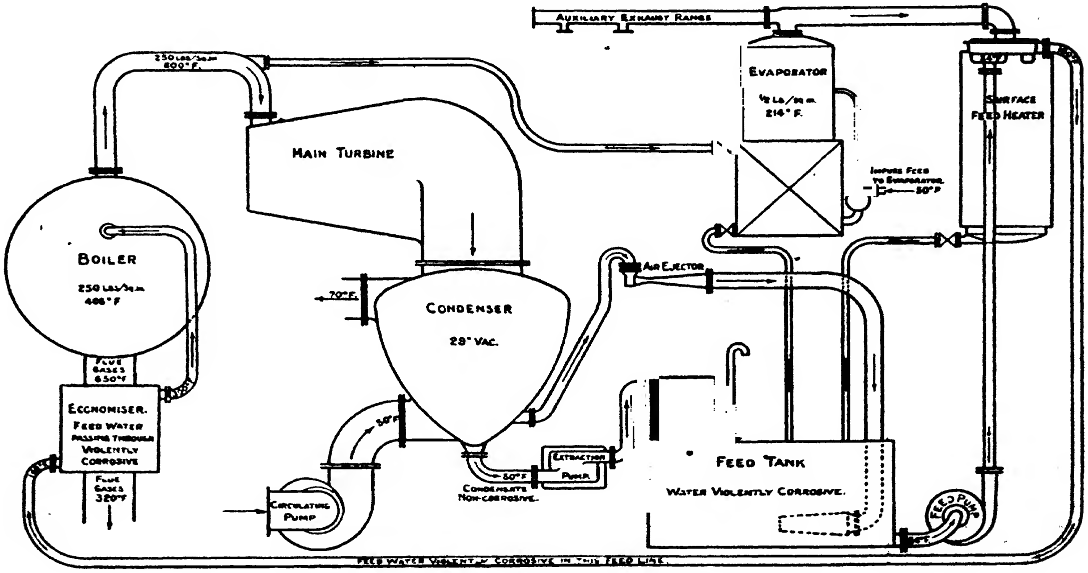
Auxiliary Exhaust Range
Evaporator
½ Lb/sq in.
214° F.
Surface Feed Heater
Impure Feed to Evaporator 50° F
250 Lbs/sq in.
800° F.
Main Turbine
Boiler
250 Lbs/sq in.
406° F
Air Ejector
70° F.
Condenser
29" Vac.
Flue Gases 650° F
Economiser. Feed Water passing through Violently Corrosive
Flue Gases 320° F
50° F
Extraction Pump
50° F
Condensate Non-corrosive.
Feed Tank
Water Violently Corrosive.
Circulating Pump
Feed Pump
Feed Water Violently Corrosive in this Feed Line.

Fig. 37.—Usual Arrangement of an "Open-Feed" System.

the condensers and discharged into the feed tank or hot well, from whence the boiler feed pump delivers it through the economisers to the boilers (see fig. 37). In the feed tank, the water is openly exposed to the atmosphere and therefore absorbs oxygen and carbon dioxide from it in amounts varying with its temperature and rate of flow through the feed tank. The water is thus able to acquire corrosive constituents or to supplement those already present in it, resulting, for instance, from aëration in the pumps due to imperfectly sealed glands. With the usual arrangements, therefore, in which hot wells and other storages are exposed, the water is contaminated with dissolved atmospheric gases and corrosion troubles will be experienced in the feed-heaters, economisers, and other units as a result. This unsatisfactory circulation system may be obviated by a slight modification in the system and the installation of a degasser, such, for instance, as the Weir Direct Contact Heater. Instead of the condenser extraction pumps discharging into the feed tank, they are arranged to discharge into the degasser. This is supplied, as already described, with auxiliary exhaust steam, and the pressure inside it is reduced by means of a pipe connection to the main condenser. The de-aërated water from the heater flows by gravity to the suction of a booster pump of the centrifugal type, by which it is discharged direct to the feed pump and thence to the boilers. By this arrangement, the feed-water, after leaving the heater, is prevented from exposure in any way to the atmosphere or other gaseous pressure and the boilers receive it, therefore, in a gas-free condition. The conversion in this way of an existing plant of the " open " type to one of the " closed feed " type is shown in fig. 38.

In erecting a new station it is possible and desirable to arrange the feed system at the outset so that all corrosive gases are removed from the make-up water at the earliest possible moment after its entry into the circulation system and to ensure also that the feed has no opportunity of absorbing gas at any point of the cycle. Arrangements which fulfil these desiderata are well illustrated in fig. 39, which shows the application of the Weir Closed Feed System. The make-up passes directly from the feed tank into the condenser through a pressure control valve, and in the condenser is exposed, together with the condensate, to a vacuum corresponding to the water temperature. The make-up water is thus boiled and the gases which are driven off are immediately withdrawn by an air-ejector which is operating continuously on the condenser. These conditions are extremely favourable to very thorough de-aëration of the make-up water; the temperature of the latter is usually much higher than the condenser temperature and the sudden injection of the warm make-up into the condenser, where the pressure is low, results in a rapid liberation of the dissolved gases. The whole feed supply is therefore boiled in the condenser under conditions which, as already stated, are very favourable to de-äeration; the condenser is, in fact, made to function as a degasser, the gases released in it being discharged by an air ejector from the circulation system into the atmosphere.

Another typical de-aëration process is that of the Elliott Co., Pittsburgh. Heated water is injected into a vacuum in which the vapour temperature is materially below the temperature of the incoming water. On entering the vacuum chamber, violent boiling occurs at the expense of the available heat in the water, some of which is

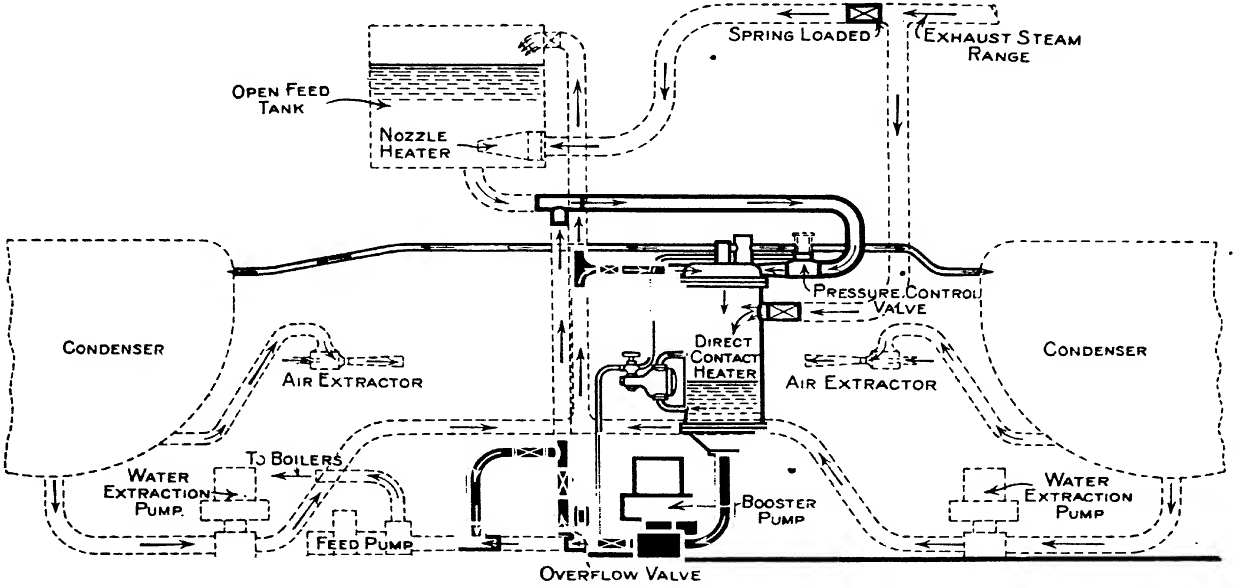
Open Feed Tank
Nozzle Heater
Spring Loaded
Exhaust Steam Range
Condenser
Air Extractor
Pressure Control Valve
Direct Contact Heater
Air Extractor
Condenser
To Boilers
Water Extraction Pump
Feed Pump
Overflow Valve
Booster Pump
Water Extraction Pump

Fig. 38.—Conversion of an "Open-Feed" System to a "Closed-Feed" System and Installation of a Weir Direct Contact Heater.

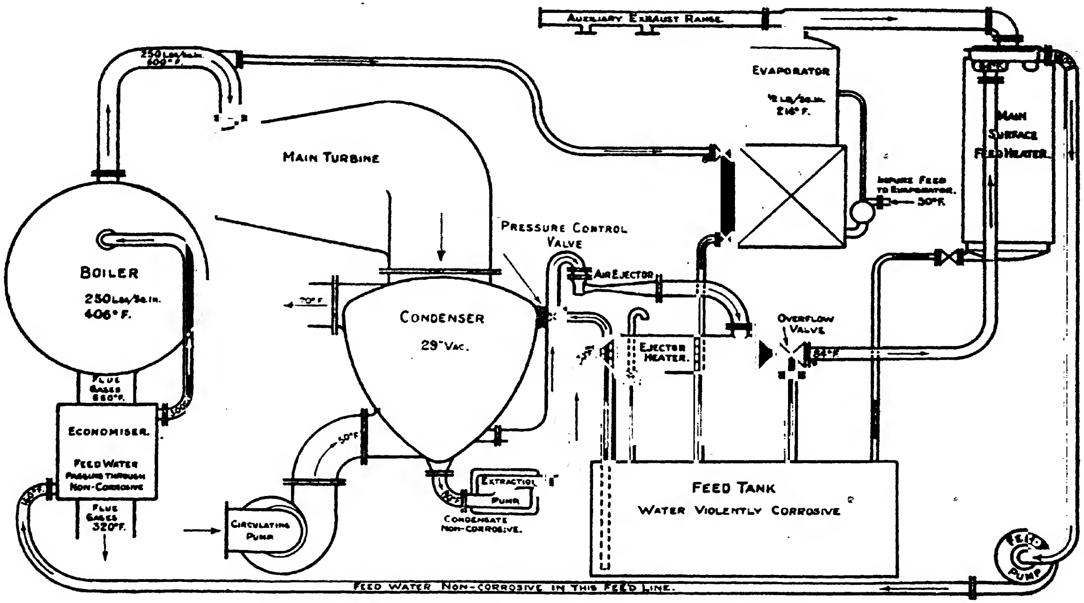
Auxiliary Exhaust Range
250 Lbs/Sq. In.
406° F.
Main Turbine
Evaporator
½ Lb/Sq. In.
216° F.
Main
Surface
Feed Heater
Impure Feed
to Evaporator.
50° F.
Pressure Control
Valve
Air Ejector
Boiler
250 Lbs/Sq. In.
406° F.
70° F
Condenser
29" Vac.
Overflow
Valve
84° F
Ejector
Heater.
Flue
Gases
660° F.
Economiser.
Feed Water
Passing Through
Non-Corrosive
100° F
50° F
Extraction
Pump
80° F
Condensate
Non-Corrosive.
Feed Tank
Water Violently Corrosive
Flue
Gases
320° F.
Circulating
Pump
Feed
Pump
160° F.
Feed Water Non-Corrosive in this Feed Line.

FIG. 39.—ARRANGEMENT OF THE WEIR "CLOSED-FEED" SYSTEM.

converted into steam. The dissolved gases are given up and exhausted by an air ejector from a condenser which recovers the heat liberated as described above by transferring it to the incoming water. The apparatus consists of a heater, A, for heating the water, a separator, B, for de-aërating the water, a condenser, C, for recovering the heat and vapour liberated during the de-aëration, and an air ejector, D, for maintaining the vacuum. The units may be built integrally as shown in fig. 40, which illustrates the vertical type of Elliott degasser, and in figs. 41 and 42, showing the horizontal type, which latter comprises the large installations handling quantities of water in excess of 150,000 pounds per hour. The water to be degassed passes through the condenser and then flows to the heater, where it is heated to the required temperature. From the heater it is delivered to the separator or the degasser, where explosive boiling takes place due to the reduced pressure. Most of the water passes through the separator and is handled by the pump suction, but some of it is converted into steam, and this steam, together with the air liberated from the water, passes into the condenser, where the steam is condensed and its heat returned to the entering feed-water. The gases are removed by the air ejector, and the condensed steam in the surface condenser runs back into the separator by gravity. It may be advisable in some cases to use a jet condenser instead of a surface condenser, for instance, where the temperature of the water supply is too high for condensing purposes. Under these conditions the condensed steam will, of course, be mixed with the cooling water and the whole is therefore returned to the heater. A large Elliott degassing installation is shown in the frontispiece. Fig. 43 shows the application of the Elliott de-aëration process to hot-water service lines in hotels, etc., and is sufficiently self-explanatory as to require no further comment.

The treatment of the subject of degassing might well be elaborated very considerably, but since it constitutes only one section of the problem with which we have to deal, the foregoing description of the methods or processes in vogue is felt to be sufficiently comprehensive without being unduly out of proportion with regard to other sections.

ELECTROLYTIC METHODS OF PREVENTING CORROSION

The practice of inserting zinc slabs in boilers is well known and has achieved a certain amount of popularity. Theoretically the practice is a sound one. If good electrical contact is made between the zinc and the metal of the boiler there is formed a " couple " of dissimilar metals of which the zinc is the electro-positive component. Any corrosive tendency on the part of the water will therefore result in the preferential solution or corrosion of the zinc, and the iron boiler shell and tubes will be protected at the expense of the latter. The electrolysing or galvanic currents, which effect the solution of the metal, flow from the zinc into the electrolyte or boiler water and from the boiler water into the boiler metal. The boiler-metal acts, therefore, cathodically, and as long as this condition exists it does not corrode. There are, however, several serious objections to this practice. Chief amongst these is the reversal of polarity between the surfaces of the zinc slabs and the iron of the boiler. After a time the zinc becomes covered with a deposit, either of its own corrosion

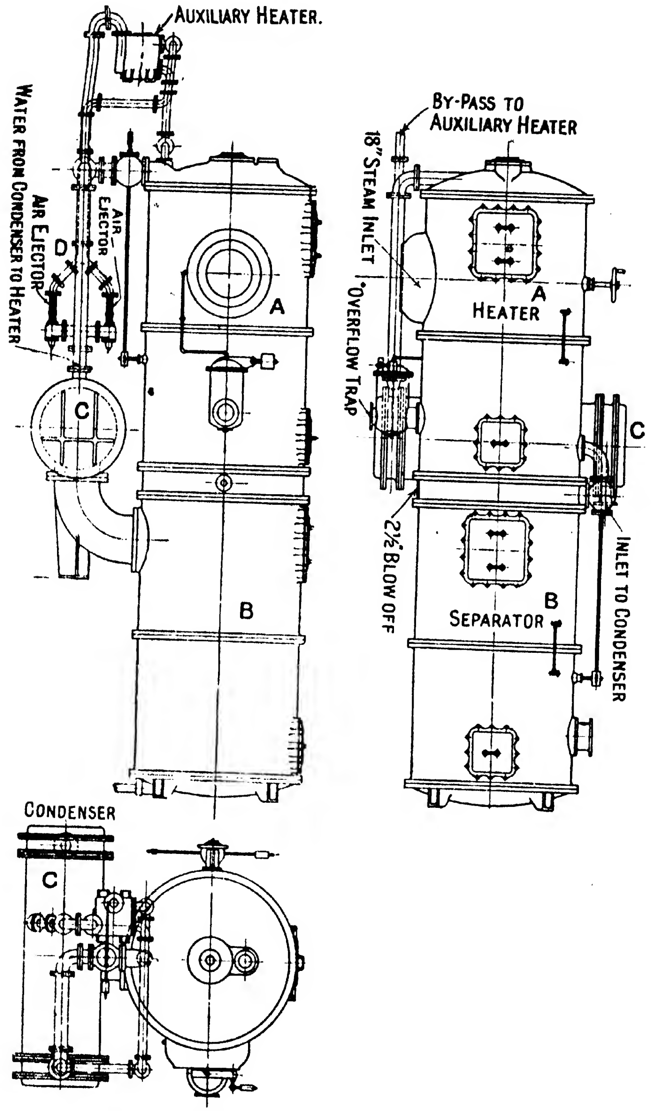
AUXILIARY HEATER.
WATER FROM CONDENSER TO HEATER
AIR EJECTOR
D
AIR EJECTOR
A
C
B
CONDENSER
C
BY-PASS TO AUXILIARY HEATER
18" STEAM INLET
OVERFLOW TRAP
A
HEATER
C
2½ BLOW OFF
B
SEPARATOR
INLET TO CONDENSER

FIG. 40.—ELLIOTT PHYSICAL DEGASSER. VERTICAL TYPE.

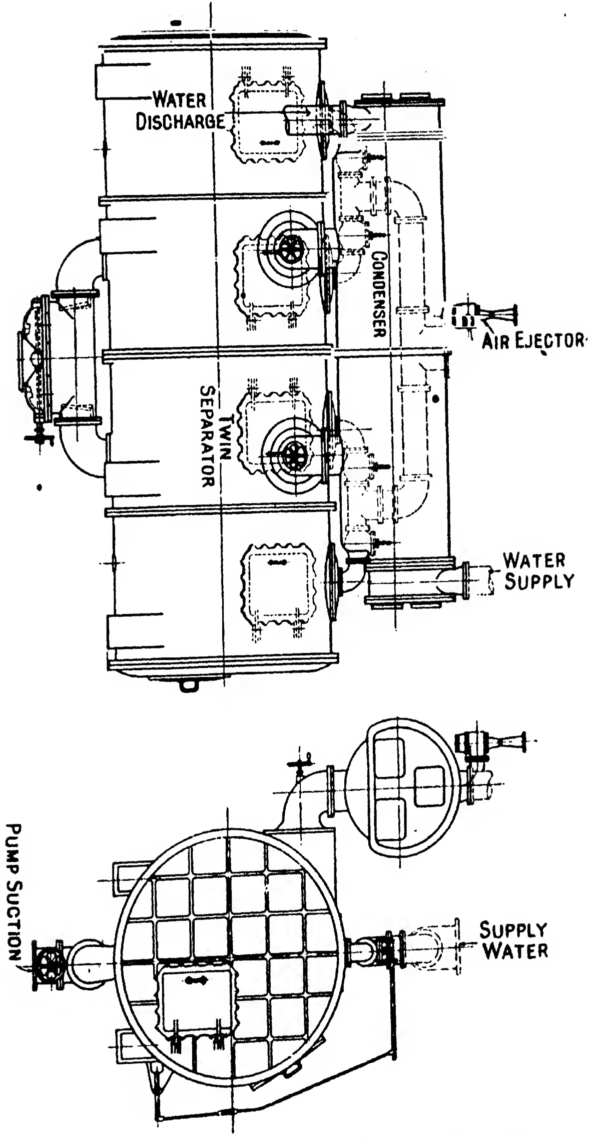
WATER DISCHARGE
CONDENSER
AIR EJECTOR
TWIN SEPARATOR
WATER SUPPLY
PUMP SUCTION
SUPPLY WATER

FIG. 41.—ELLIOTT PHYSICAL DEGASSER. HORIZONTAL TYPE.

products or of scale-forming matter from the water, and this material, instead of being electro-positive to the iron, as is the zinc itself, is electro-negative. As a result, the object aimed at in providing the zinc slabs is defeated, and, worse than this, the corrosion of the boiler may be actually accelerated by their presence. Added to this is the difficulty of securing and maintaining a good electrical contact between the zinc and the boiler and the frequent renewals of the expensive zinc plates which are necessary. Further, in a modern boiler the zinc cannot be placed indiscriminately inside it, but is necessarily located in those portions where sufficient space is available, and, since its influence is restricted to a limited sphere, the parts of the boiler beyond this sphere receive no protection. Protection by means of zinc plates would

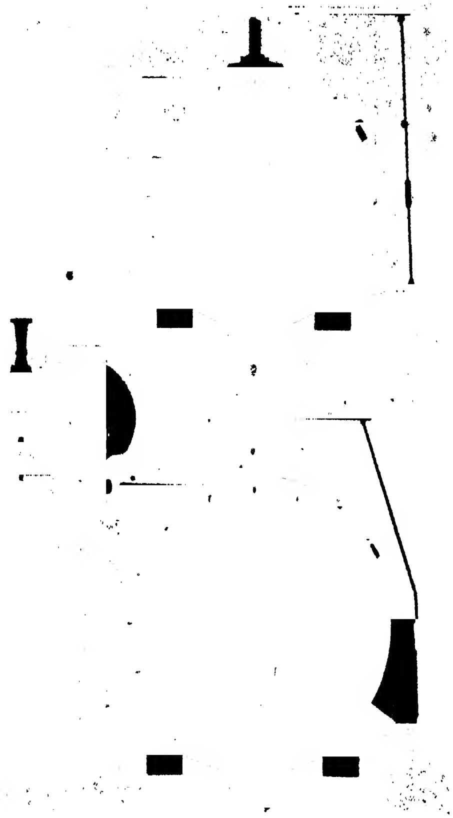

FIG. 42.—ELLIOTT HORIZONTAL DEGASSER, LARGE UNIT.

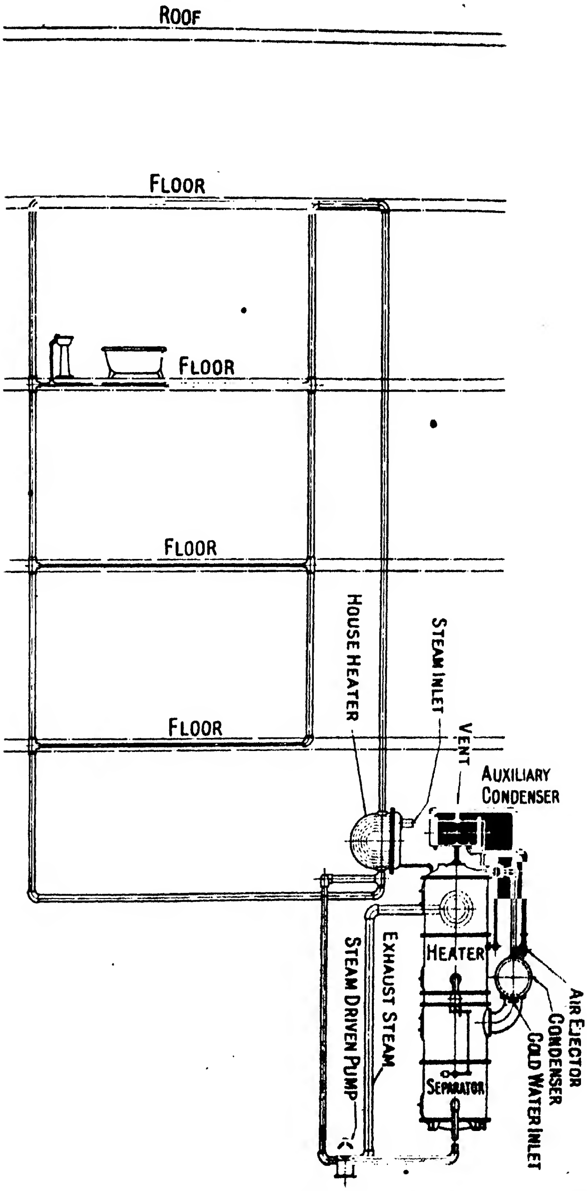
ROOF
FLOOR
FLOOR
FLOOR
FLOOR
HOUSE HEATER
STEAM INLET
VENT
AUXILIARY CONDENSER
HEATER
SEPARATOR
EXHAUST STEAM
STEAM DRIVEN PUMP
AIR EJECTOR CONDENSER
COLD WATER INLET

Fig. 43.—Elliott de-Aëration System Applied to Hot Water Service Lines.

not, therefore, appear to merit the popularity which it enjoys amongst certain sections of practical engineers. It would appear to have become a fetish. As mentioned above, it is sound enough in conception, since it does initially oppose a higher potential to that tending to corrode the metal, but it fails solely because it does not maintain this opposing electromotive force.

The best method of applying electrolytic protection, whether to boilers, economisers, condensers, etc., is that known as the Cumberland Electrolytic System. Here, again, the beneficial effects of a counter E.M.F. are recognised, but, in addition, the necessity for arrangements whereby this may be permanently maintained are also recognised and the reversal of polarity, which may occur with zinc slabs, is effectively prevented. Briefly, the equipment comprises a low-voltage external generator which supplies current to a number of iron bar anodes, suitably disposed in and insulated from the boiler or condenser which is to receive protection. The opposing current flows, therefore, from these insulated anodes, through the water into the metal shell and tubes of the boiler, which act cathodically and is connected electrically with the negative pole of the generator. Apart from the initial outlay, the cost of upkeep is confined to the renewal of the iron anodes, which are cheap in comparison to the zinc slabs, and their renewal is facilitated by the provision of specially designed insulated holders which can be readily removed and replaced. The counter E.M.F. is generated by a rotary transformer of suitable capacity operated from a lighting or power circuit.

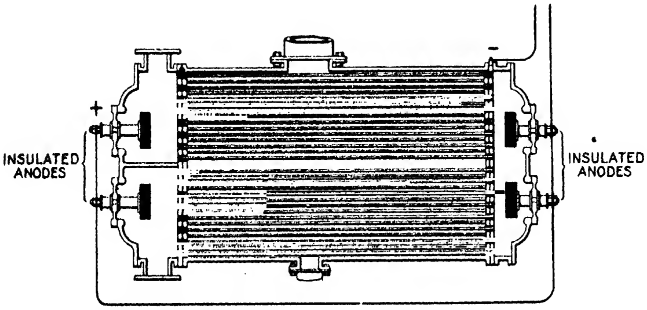

Fig. 44.—Application of the Cumberland Electrolytic Protection to a Surface Condenser.

Figs. 44, 45, and 46 show the arrangement of the anodes as disposed in marine boilers of the Yarrow type, in condensers, and in economisers. It is also of interest to note that the application of this system of protection has the effect of detaching old scale from boiler surfaces, so that it can be removed as sludge in the blow-down, and of preventing the formation of scale on clean surfaces.

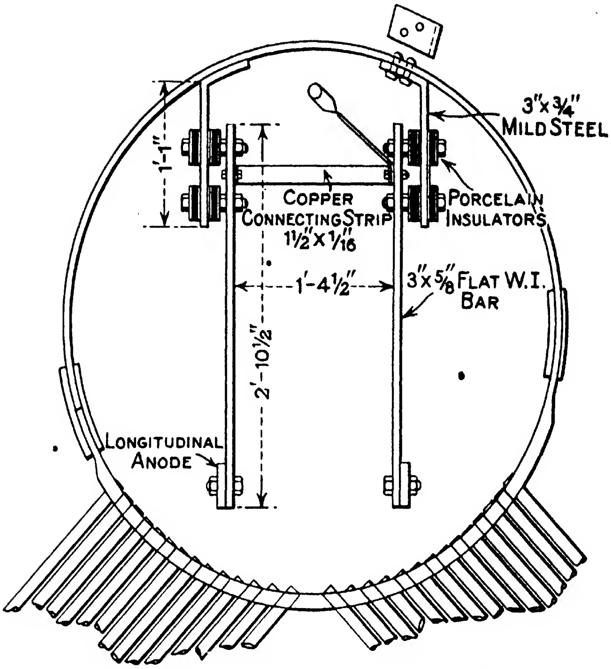
3"x¾"
Mild Steel
1'-1"
Copper
Connecting Strip
1½"x1/16"
Porcelain
Insulators
1'-4½"
3"x⅝" Flat W.I.
Bar
2'-10½"
Longitudinal
Anode

Fig. 45.—Application of the Cumberland Electrolytic Protection to a Yarrow Boiler.

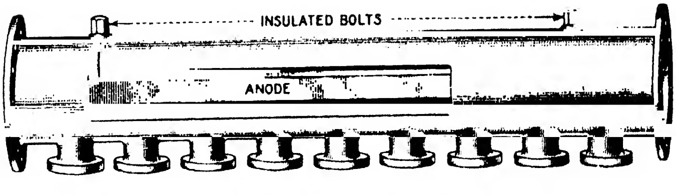
INSULATED BOLTS
ANODE

Fig. 46.—Application of the Cumberland Electrolytic Protection to Economiser Tubes.

SUMMARY OF THE BEHAVIOUR AND REMOVAL OF THE IMPURITIES IN NATURAL WATERS

Alumina and Suspended Matter.—The quantities of these vary considerably according to locality and seasonable influences. If they are finely divided they may cause priming, and this, together with the fact that if the quantity is large it may cement precipitated boiler sludge into a hard scale, is the chief objection to it. The elimination of this kind of impurity is effected by filtration or sedimentation.

Ammonium Salts.—The presence of these salts in water is due usually to industrial contamination, such as from coke ovens, gas plants, etc. Ammonium salts are non-scale-forming, but are very corrosive. They dissociate into free ammonia, which is carried away by the steam, and free acid. Extensive and serious damage may result in a very short time by using, as boiler feed, a water containing these salts. The effect of other forms of industrial pollution can often be anticipated from a consideration of their nature, *i.e.* whether they are acid or alkaline or readily dissociated salts such as the ammonium salts, ferrous sulphate, etc.

Calcium Carbonate.—This impurity originates from the natural crystalline form of marble and limestone and from the amorphous form of chalk, and is present in the large majority of natural waters in this country. The normal carbonate is practically insoluble in water, but in the presence of free dissolved carbon dioxide it is soluble in large quantities as the bicarbonate and is a cause of temporary hardness. On boiling its solution, free carbon dioxide is evolved and the normal carbonate of lime is precipitated. It forms a soft scale and sludge in the boilers when alone, but in conjunction with certain other precipitated material may give rise to a hard scale. It is not corrosive except indirectly by reason of the liberation of carbon dioxide which accompanies its deposition. Most natural waters contain more or less of this impurity, which may be removed either by treatment with lime or by filtration though an artificial zeolite, or by treatment in a hot-process softener whereby carbon dioxide is removed.

Calcium Chloride.—This salt is rarely found in natural waters. It may often appear in boiler waters, however, as a result of interaction between calcium carbonate and magnesium or sodium chloride, or through an excess of calcium chloride being used in a softener designed to reduce the sodium carbonate content of the water. Contamination with sea-water, as may occur in ship's sets, will also lead to the development of troubles due to chloride of lime. It is not itself a scale-forming impurity, but in conjunction with magnesium sulphate may give rise to a sulphate of lime scale, magnesium chloride being produced at the same time by the exchange of radicles. It is corrosive, however, and may, so far as the boiler plates and tubes are concerned, be regarded as hydrochloric acid. Treatment with sodium carbonate is usually adopted to eliminate it, its place being taken by sodium chloride.

Calcium Nitrate.—This occurs in waters in which oxidation of organic matter has proceeded and as a result of which nitric acid has been produced. The oxidation of organic matter is also the cause of the presence of this salt in soils, from whence it can find its way into water supplies. It is a permanently soluble salt, *i.e.* is not precipitated in the boilers, and is very corrosive. It attacks the metal, being itself reduced to nitrite and at the same time free lime is also produced and may be sufficient to impart a deceitful alkalinity to the boiler water. If sulphate of soda is also present in the water, a sulphate of lime scale may be produced. The removal of calcium nitrate is effected similarly to that of calcium chloride, but in this case, of course, an equivalent of sodium nitrate is introduced into the water.

Calcium Nitrite.—Probably this salt is always produced on site, by the reduction of the nitrate in the boilers. As it still contains, or retains, oxidising properties, it may be regarded as detrimental. All calcium salts other than the carbonate are sources of permanent hardness.

Calcium Sulphate.—Natural waters contain this salt as the hydrated sulphate. The anhydrous salt is insoluble, and as the water of hydration is given up at about 260° F., the salt is precipitated in the boilers. It forms a very objectionable scale, very hard and firmly adherent to the metal upon which it is deposited. It is not commonly found as a predominating constituent in economiser tube scales. Softening processes remove it by means of sodium carbonate, the carbonate of lime is precipitated and an equivalent amount of the comparatively harmless sodium sulphate replaces the original sulphate of lime.

Dissolved Gases. Oxygen and Carbon Dioxide.—Carbon dioxide occurs in all natural waters in quantities sufficient to keep the carbonates of lime and magnesia in solution as the bicarbonates. Frequently the amount is considerably in excess of this. The whole of this gas is set free in the boiler, both the semi-combined and the free dissolved portions, and whilst opinions differ as to the relative corrodibilities of this gas and oxygen, there can be no question that its presence is certainly not beneficial and there is much evidence to show that, if its quantity is large, any corrosion proceeding from other causes is accelerated. It may be removed by boiling, by means of lime in a softening plant or by deactivation or degassing. Oxygen is now regarded as the most common and the most active corrosive constituent of water. It is present in all natural waters, the quantity varying with the nature of the source of the water and the mode of its collection, storage, and circulation. Its elimination is effected either by evaporation (distillation) or by degassing processes. The other dissolved gas, nitrogen, which is also invariably present, is of no significance.

Hydrogen Sulphide.—This is sometimes found in spring waters in certain localities. The chief objection to it is that it may become oxidised to sulphuric acid. It rarely occurs in boiler feed-waters, however, and no standard process for its elimination appears to have been put forward.

Iron and Aluminium Salts.—Traces of these salts are usually found in natural waters and normally they are disregarded. When iron is present in any quantity, it is usually in the form of ferrous sulphate, which is very corrosive. It hydrolyses in the boilers to ferrous hydroxide and free sulphuric acid. Aluminium salts behave in a similar manner, producing hydrated alumina and the free acid. These salts are removed by treatment with lime or sodium carbonate or by oxidation. The reagent used to reduce the quantity of sodium carbonate in waters in which this salt is present in large amounts is alum, but sometimes a commercial product, known as alumina-ferric, may be used. This contains varying percentages of sulphate of iron as wel as the sulphate of alumina, and if the water is over treated both these salts may finc their way into the boiler. Aluminium sulphate is rarely found in natural waters, but the iron salt is more frequently present.

Magnesium Carbonate.—This originates from magnesian limestones, etc. Like the lime salt, it is very soluble in waters containing dissolved carbon dioxide. It decomposes under boiler conditions, first into the normal carbonate and then into magnesia, and is not directly either scale-forming or corrosive. The carbon dioxide evolved during its precipitation as sludge is corrosive, however, and in the presence of any chloride in the water the magnesia itself becomes actively and violently corrosive by becoming converted into the magnesium chloride. The precipitated magnesium hydrate usually remains as sludge, and is a source of priming troubles. Occasionally it may be found as a very hard, heat-insulating scale. Treatment with lime will remove it from the feed-water, but the lime must be in sufficient quantity to convert the magnesium bicarbonate beyond the normal carbonate, which is appreciably soluble in water, to the insoluble hydrate. Its removal adds nothing to the concentration of soluble salts in the treated water. Magnesium carbonate causes temporary hardness similarly to calcium carbonate.

Magnesium Chloride.—This very soluble salt is looked upon as the worst possible impurity a boiler water can contain. It occurs in many natural waters and is produced in the boilers whenever the water contains a magnesium salt and other chlorides. Even dilute solutions are very corrosive, and its concentration in the boiler can only be reduced by blowing down. Its corrosive action on the boiler metal may be explained by a cycle of reactions in which hydrochloric acid is being continually passed backwards and forwards between the magnesium and the iron. When the concentration of the salt is excessive its corrosive influence may be transmitted by the steam to the superheaters, turbines, etc. A lime-soda treatment is employed to remove it from boiler-feed.

Magnesium Nitrate.—The occurrence of this salt in natural waters is due to the same causes which occasion the presence of calcium nitrate in them. Its behaviour in the boiler is in every way comparable with that of the corresponding lime salt.

Magnesium Sulphate.—The danger attached to the presence of this salt lies in the reactions which can take place between it and other salts also present. Thus it may indirectly cause both scale and corrosion. If chlorides are present it may be looked upon as magnesium chloride, and since these are rarely, if ever, absent, magnesium sulphate must be classed as a corrosive salt. It is very soluble in water and adds to the permanent hardness figure, as do all magnesium salts with the exception of the carbonate. It is removed by a lime-soda treatment; magnesium carbonate is first produced by reaction with the soda, and then this is converted to the hydrate by the lime. In common with all soluble salts it is, of course, replaced by sodium sulphate.

Silica.—Silica is normally soluble to the extent of about one-quarter of a grain per gallon, and is usually found in small quantities in waters. It is much more soluble in alkaline waters, and these may contain relatively large amounts of silica dissolved as sodium silicate. It may, of course, also be present in suspension, and if the water containing it in this form is softened by a lime-soda treatment, a considerable proportion of this silica may be brought into solution by the sodium carbonate. A similar result will be obtained if the lime used in the softener contains much silica as impurity. Silica is virtually an acid, and as such merits special attention. It can, under boiler conditions, replace other acids, and these latter are liberated in the free condition, whilst, at the same time, the silicates formed may produce a particularly objectionable scale. Further, if these reactions take place, as is most probable, on the metal surfaces, the liberated acids can set up corrosion underneath the scale. The advisability of removing silica will depend upon the general characteristics of the water. Normally occurring amounts may be neglected as a rule, but if the water is alkaline and contains also calcium and magnesium salts it may be necessary to treat it. The silica may be removed by acidifying the water, filtering, and then re-softening with sodium carbonate, but the process does not appear to be very often applied. Silica may in some cases be present in large quantities in the colloidal or hydrated form.

Sodium Carbonate.—This is often found in natural waters, particularly those obtained from deep and artesian wells. Its presence indicates that the water has percolated through a stratum of natural zeolite. In certain cases its presence in boiler waters may be attributed to incorrect proportioning of the softening reagents whereby an excess of soda passes through the filters with the treated water. A low concentration of this salt is perhaps desirable in a boiler water, as it gives sufficient alkalinity to retard or prevent corrosion. Should its concentration become high, however, troubles may be experienced; it is often held responsible for priming and it corrodes non-ferrous boiler fittings. It is also decomposed in up-to-date plants, where the pressures are high, into caustic soda and a number of other products, more or less definitely established, and of an organic character. In such cases it would appear to be responsible for a high dissolved oxygen content in the condensate, and this alone is sufficient to justify its concentration being kept within reasonable limits, say below 25 to 30 grains per gallon. The boiler-feed may be treated with alum or calcium chloride to convert the sodium carbonate into the sulphate or chloride respectively.

Sodium Chloride.—This salt is invariably present in waters and cannot be removed by treatment in a softening plant. It is, of course, soluble, and is non-scale-forming and is also usually considered as non-corrosive. This latter is, however, open to criticism, since experience tends to show that if corrosion is proceeding, its rate is normally accelerated by the presence of common salt. It is chiefly to be avoided when magnesium salts are also present, and this is effected by treating the water so as to remove the latter. If this were not done, the corrosive magnesium chloride would be formed in the boilers. With sodium chloride as the predominating impurity, however, the only thing to be guarded against is its undue concentration, and the blow-off is generally the only means available.

Sodium Hydrate.—If this is present in a boiler it is usually due to over treatment in the softener or to the decomposition of sodium carbonate in cases where the concentration of this salt is high. A small quantity is beneficial and is probably the most satisfactory form of alkali to have in the boilers, but its amount must be kept low.

Sodium Nitrate.—This is seldom found in natural waters in large quantity. It will usually occur in boiler waters as a result of the removal of the more dangerous nitrates of lime and magnesia. Unless its concentration is allowed to become unduly high, it is, at any rate, a lesser evil than the alkaline-earth nitrates. Nevertheless it is corrosive and its concentration should therefore be watched. In conjunction with lime or magnesium salts in unsoftened water, it is, of course, virtually equivalent to magnesium or calcium nitrate.

Sodium Sulphate.—In treated water this is generally regarded as harmless, and probably correctly so. In unsoftened water containing soluble calcium salts, for instance, it may be indirectly responsible for the production of a sulphate of lime scale. It cannot be removed by any softening process, and its concentration in the boiler can only be controlled by the blow-off cock. Excessive amounts may result in the formation of a sulphate of soda scale. The salt is itself apparently non-corrosive. High concentrations of it are sometimes held responsible for priming, but it is probably no worse in this respect than would be any soluble salt if its concentration were sufficiently high.

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INDEX

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INDEX

Abrasions, effect of, on corrosion, 75.
Acetaldehyde, formation in boilers, 102.
Acetone, formation in boilers, 102.
Acid, chromic, action on iron, 59.
  fumes, protection against, 137.
  hydrochloric, action on iron, 57.
  media, influence on corrosion, 57
  nitric, action on iron, 59.
  phosphoric, action on iron, 58.
  sulphuric, action on iron, 58.
  theory of corrosion, 15, 24.
Acidity of soils, 47.
Air, action on iron, 45.
Alkaline media, action on iron, 59.
  waters, 84.
Alkalinity of boiler water, 100.
Alumina in feed-water, 218.
Aluminium coatings, 151.
  effect on corrosion, 67.
  salts, removal of from water, 177
  sulphate in boiler feed, 100.
Ammonia in water, 79.
Ammonium salts in boiler feed, 100
    removal of, from water, 218.
  sulphate, source of, in water, 81
Angus Smith process, 164.
Animal oils, 55.
Annealing condenser tubes, 126.
Anti-fouling paints, 163.
Arsenic, effect on corrosion, 67.
Artesian-well water, 82.
Asbestine, 157, 163.
Atmospheric impurities, 54.
Auto-corrosion, 34.
Auto-electrolysis, 35.

Barff process, 136.
Barium chromate, pigment, 166.
  sulphate, pigment, 166.
Barytes, 166.
Biological theory of corrosion, 32.
Bituminous coatings, 164.
Blow-down, method of, 93.
Blue lead, pigment, 166.
Boiler compounds, 178.
  troubles, 90.
Boiler water, alkalinity of, 100.
    corrosive matter in, 87.
Boilers, bumping of, 91.
  chemical reactions in, 96.
  dissociation of salts in, 87.
  evolution of oxygen in, 101.
  formation of acetaldehyde in, 102.
    of acetone in, 102.
    of hydrochloric acid in, 98.
    of lactic acid in, 102.
    of organic compounds in, 101.
    of sodium acetate in, 102.
    of sodium formate in, 102.
    of sugars in, 102.
  priming of, 91.
  scale and corrosion in, 94.
Bone black, pigment, 166.
Bontempi process, 138.
Bower-Barff process, 136.
Bradley process, 138.
Brass, products of corrosion of, 109
Bumping, causes of, 91.
Buried iron, corrosion of, 34, 65.
Busy iron, corrosion of, 76.

Calcium carbonate, in feed-water, 218
    in soil, 47.
    pigment, 167.
  chloride, in feed-water, 99, 218.
  nitrate, in feed-water, 99, 218.
    source of, in water, 80.
  nitrite, source of, in water, 80.
  sulphate, in feed-water, 219.
    in soils, 47.
    pigment, 167.
    precipitation of, in boilers, 96.
    solubility of, 88.
    source of, in water, 78.
Calorising process, 151.
Carbon, influence of, on corrosion, 64.
  black, pigment, 167.
  dioxide, action of excess on iron, 27, 102.
    in atmosphere, 54.
    in water, 79.
    occluded in iron, 71.
  hardening, 65.

Carbonic acid, 25, 58.
Cast iron, graphitisation of, 65.
Cellulose acetate, in waters, 84.
  products from in water, 84.
China clay, 167.
  Wood oil, 159.
Chromic acid, action on iron, 59.
Chrome Green, pigment, 167.
  Yellow, pigment, 168.
Chromium, effect of, on corrosion, 67.
Cinder inclusions, 71.
Cobalt, effect of, on corrosion, 68.
Cold-working, effect of, on corrosion, 75
Colliery waters, 84.
Colloidal solutions, 28.
Colloids, catalysing, 31.
  emulsoid, 29.
  migration of, 29.
  positive and negative, 29.
  precipitation of, 29.
  properties of, 28.
  suspensoid, 29.
Colloid theory of corrosion, 30.
Concentration cells, 72.
Condensate, dissolved oxygen in, 88.
Condenser tube corrosion, factors influencing, 108.
      types of, 107, 112.
    failure, causes of, 111.
  tubes, accumulation of corrosion products in, 115.
    acid cleaning of, 124.
    action of sea water on, 108.
    "complete" corrosion of, 112.
    electrical leaks, 117.
    electrolytic protection of, 121.
    faulty composition of, 113.
    ferrule troubles, 119.
    foam formation in, 117.
    foreign substances in, 116.
    iron in, 114.
    iron compounds in, 120.
    laminations in, 113.
    lead in, 114.
    manganese in, 114.
    mechanical cleaning of, 124.
      failure of, 115.
    nickel in, 114.
    oxidising annealing of, 126.
    prevention of corrosion of, 121.
    protection of, by insoluble salts, 126.
      of, by metallic layers, 126.
    "selective" corrosion of, 112.
    subsidiary steam supplies in, 116.
    tin in, 114.
    top inlet deterioration, 116.
Condenser tubes, water-end design, 119.
  water speed, 117.
Contact corrosion, 35.
Continuous blow-down, 191.
Copper, effect of, on corrosion, 68.
  protective coatings of, 151.
Corrodibility, comparative, of modern metals, 134.
  relative, of iron and steel, 37.
Corrosion, acid theory of, 24.
  accelerated by rust, 52.
  auto-, 35.
  biological theory of, 31.
  brass, of, 36.
  buried iron, of, 34, 65.
  busy iron of, 76.
  in boilers, 94.
  colloid theory of, 30.
  contact, 36.
  definition of, 14.
  electrolytic prevention of, 211.
    theory of, 15, 24.
  effect of aluminium on, 67.
    of arsenic on, 67.
    of chromium on, 67.
    of cobalt on, 68.
    of copper on, 68.
    of lead on, 70.
    of light on, 49.
    of manganese on, 66.
    of mill-scale on, 70.
    of nickel on, 69.
    of phosphorus on, 66.
    of silicon on, 65.
    of sulphur on, 66.
    of temperature on, 50, 61.
    of tin on, 70.
    of tungsten on, 70.
    of vanadium on, 70.
  externally induced, 34.
  factors affecting, 44.
  in excess of carbon dioxide, 27, 102.
  in stagnent water, 49.
  in moving water, 30.
  influence of acid media on, 57.
    of oils on, 55.
    of oxygen on, 25, 45.
    of rate of flow of water, 48.
    of salt concentration on, 31, 60.
    of segregation on, 16, 35, 66, 71.
    of strain on, 16, 37, 73.
  oxide theory of, 31.
  preferential, 36.
  peroxide theory of, 31.
  prevention of, 133.
  superheater tubes of, 46, 103.

Corrosion, theory of, 24.
  turbine blades of, 46, 104.
  types of, 34.
Corrosive constituents of waters, 78.
  salts, removal of, from water, 173.
Corrosivity of soils, 47.
Coslett process, 140.
Critical concentration of salt solutions, 60.
Crystalloids, 28.
Cumberland electrolytic protection, 34, 36, 216.

Deep-well water, 82.
Degassing, chemical, 203.
  physical, 204.
Design, care in, 134.
Dewees-Wood process, 138.
Dezincification, 36, 108, 112.
Dispersion medium, 28.
Dispersoid, 28.
Dissimilar metals, contact between, 135.
Dissociation, electrolytic, 20.
Dissolved gases, removal of, from water, 198.

Economiser scale, 88.
  troubles, 87.
  tubes, burning of, 90.
    external corrosion of, 90.
    external deposits on, 90.
Electrical leaks in condenser tubes, 117
Electro-chemical series of the metals, 36.
Electrolysis, 21.
  -auto, 35.
Electrolyte, heterogeneity of, 72.
Electrolytic dissociation, 20.
  prevention of corrosion, 121, 211.
  theory of corrosion, 25.
Erosion, 15.
Estuarine waters, selective corrosivity of, 109.
External deposits, 90.
Externally induced corrosion, 34.

Factors affecting corrosion, 44.
Feed-water, aluminium sulphate in, 100.
  ammonium salts in, 100.
  calcium chloride in, 99.
    nitrate in, 99.
  ferrous sulphate in, 100.
  grease and oil in, 93.
  magnesium chloride in, 98.
    nitrate in, 99.
    sulphate in, 99.
  sodium carbonate in, 101
    chloride in, 99
Feed-water, summary of impurities in, 218.
  treatment, 172.
Ferric hydroxide, 26.
Ferro-manganese, 67.
Ferro-silicon, 65.
Ferroso-ferric oxide, 46.
Ferrous hydrate, colloidal, 30.
  sulphate, in feed-water, 100.
  sulphide, 66.
Ferroxyl reagent, 38, 73.
Ferrule troubles in condensers, 119.
Foam formation in condensers, 117.
Formaldehyde, 27.
Formic acid, 27.

Galvanic action, 34.
Galvanised surfaces, painting of, 162.
Galvanising, hot-dip process, 145.
Gases, dissolved in water, 48, 198, 201.
  occluded in iron, 71.
  removal of, from water, 198.
Gesner's process, 138.
Graphite, pigment, 168.
Graphitic carbon, 64.
Graphitisation, 65.
Grease in feed-water, 78, 93.
  removal of, from water, 196.
Green, chrome, pigment, 167.
Grooving, of angles, etc., 75.

Hardening carbon, 65.
Hardness of water, 82.
  temporary and permanent, 83.
Heat-bluing, 140.
Heat losses due to scale, 86.
Heterogeneity, effect of, on corrosion, 35
  of electrolyte, 72.
  physical, 37, 73.
  structural, 71.
Hot-dip galvanising, 145.
Hot-process softeners, 190.
Hydrocarbon oils, 56.
Hydrochloric acid, action on iron, 57.
    formation in boilers, 98.
Hydrogen ions, 15.
  occluded in iron, 71.
  sulphide, in feed-water, 219.
Hydrolysis, 24.
Hydroxyl ions, 57.
Humic acid, 84.

Immersion, depth of, 49.
Indian red, pigment, 168.
Inhibitive factors, 76.
Internal strain, 73.
Ions, formation of, 20.

Ions, hydroxyl, 57.
  migration of, 22.
Iron, action of air on, 45.
    of steam on, 46.
    of water on, 45.
  compounds of, in condenser tubes, 120.
  in condenser tubes, 114.
  magnetic oxide of, 45.
  passive, 39.
  polished, corrosion of, 54.
  resistivity of old, 16, 134.
  salts in feed-water, 219.
    removal of, from water, 177.
  sulphate in feed-water, 100.

Japans, 163.

Kaolin, 167.

Lactic acid, formation in boilers, 102.
Laminations in condenser tubes, 113.
Lamp black, pigment, 167.
Lead, -blue, pigment, 166.
  coatings, protective, 151.
  driers, 158.
  effect on corrosion, 70.
  in condenser tubes, 114.
Light, effect of, on corrosion, 49.
Limiting concentrations, 60.
Linoxyn, 158.
Linseed oil, 158.
  adulterants of, 159.
Litharge, pigment, 168.
Lithopone, pigment, 169.
Lohmannising process, 151.

Magnesia, free in scale, 89.
Magnesium carbonate, in feed-water, 220.
    precipitation in boilers, 96.
  chloride, in feed-water, 98, 220.
  hydrate, formation in boilers, 96.
  nitrate, in feed-water, 99, 220.
  salts and priming, 92.
  sulphate, in feed-water, 99, 220.
Magnetic iron oxide, 45.
    coatings of, 136.
Manganese driers, 158.
  effect of, on corrosion, 66.
  ferro-, 67.
  in condenser tubes, 114.
  sulphide, 66.
Manufacture of metals, care in, 133.
Marine structures, painting of, 161.
Metal structures, care in design of, 134.
Metallic protective coatings, 143.
Metals, contact between dissimilar, 135.
Metals, corrodibility of modern, 134.
  electro-chemical series of, 36.
Mill-scale, effect of, on corrosion, 70.
Mineral acids in water, 78.
  black, pigment, 169.

Negative ions, precipitation of colloids by 61.
Nickel coatings, 151.
  effect of, on corrosion, 69.
  in condenser tubes, 114.
Nitric acid, action on iron, 59.
Nitrous and nitric acids in water, 79.

Occluded gases in iron, 71.
Ochre, pigment, 169.
Oil driers, 158.
Oils, animal and vegetable, 55.
  and foam formation in condensers, 118.
  hydrocarbon, 56.
  influence of, on corrosion, 55.
  organic acids from, 55.
Oily scums in boilers, 92.
Orange mineral, pigment, 169.
Organic acids in water, 78.
  compounds in water, 81.
    formation in boilers, 101.
Osmotic pressure, 19.
Oxidation, 23.
Oxide coatings, 136.
    Barff, 136.
    Bontempi, 138.
    Bower-Barff, 136.
    Bradley, 138.
    Dewees-Wood, 138.
    electrolytic, 139.
    Gesners, 138.
    Ruffington, 138.
    Wells, 138.
  theory of corrosion, 32.
Oxidising annealing of condenser tubes, 126.
Oxygen, action of, in corrosion, 45.
  depolarisation by, 26.
  dissolved in condensate, 88.
    in water, 78, 198, 202.
  essential to corrosion, 26.
  evolution in boilers, 101.
  occluded in iron, 71.
  removal of from water, 198.
  solubility of, in water, 50, 202.
  supply of, to corrosion, 48.

Paint, anti-fouling, 163.
  choice and application of, 161.
  essential properties of, 157.
  function of, 156.

Paint, materials, 105.
Painting of galvanised material, 162.
  of marine structures, 163.
  treatment of metal prior to, 161.
Parker process, 142
Passive iron, 39.
    properties of, 40.
Passivity, theories of, 40.
Peaty waters, 84.
Permanent hardness, 83.
    removal of, 173.
Permutit softening process, 194.
Peroxide theory of corrosion, 31.
Phosphide coatings, 140.
Phosphoric acid, action on iron, 58.
Phosphorus, effect of, on corrosion, 66.
Physical heterogeneity, 37, 73.
Pigments, basic and acidic, 156.
  classification of, 159.
  conducting and insulating, 160.
  effect of, on oil, 160.
  summary of, 166.
Pipe-lines, corrosion of, 65.
Pitting, 23, 36, 39, 53, 66, 71.
Polarisation, 22.
Polarity, reversal of, 39.
Polished iron, corrosion of, 54, 72.
Poppy seed oil, 159.
Preferential corrosion, 36.
Prevention of corrosion, classification of methods, 133.
Priming, causes of, 91.
Protective coatings, aluminium, 151.
    copper, 151.
    drawbacks of, 143.
    lead, 151.
    metallic, 143.
    nickel, 151.
    oxide, 136.
    phosphide, 140.
    tin, 150.
    zinc, 144.
Prussian blue, pigment, 159, 169.

Railings, corrosion of, 47.
Rain water, 80.
    corrosivity of, 48.
Rate of flow, effect of, on corrosion, 30, 77, 130.
Reactions in boilers, 96.
Red lead, pigment, 169.
Reduction, 24.
Relative corrodibility of iron and steel, 37.
River water, 81.
    self purification of, 81.
Rivet heads, pitting of, 75.
Rocks, disintegration of, 79.
Rodding out condenser tubes, 124.
Ruffington process, 138.
Rust, 51.
  accelerator of corrosion, 52.
  cones, 53.
  formation and properties of, 51.

Saline concentration, effect of, on corrosion, 31, 59.
  solutions, effect of, on corrosion, 59.
Salt in rain water, 80.
  solutions, critical concentration of, 60.
    limiting concentration of, 60.
Salts, dissociation of, in boilers, 87.
Scale, carbonate, 95.
  free magnesia in, 89.
  heat losses due to, 86.
  in boilers, 95.
  in economisers, 88.
  iron oxide, 97.
  protective action of, 88, 97.
  silicate, 95.
  sodium sulphate, 97.
  sulphate, 95.
  varieties of, 95.
Scale-forming matter in water, 78, 86.
    removal of, 173.
Schoop spraying process, 150.
Scratches, surface, 75.
Scum-forming matter in water, 86.
Sea water, action on brass, 108.
Segregation, effect of, on corrosion, 16, 22, 35, 66, 71.
Selective corrosion of condenser tubes, 112.
Selenium, effect of, on corrosion, 69.
Shallow-well water, 80.
Sherardising, 146.
  effect of iron on, 147.
  theory of, 148.
Siccatives, 158.
Sienna, pigment, 169.
Silica, 79.
  in alkaline waters, 84.
  in feed-water, 220.
Silicon, effect of, on corrosion, 65.
  ferro-, 65.
Silver, effect of, on corrosion, 70.
Slag inclusions, 71.
Sludge-forming matter in water, 86.
Sodium acetate, formation of, in boilers, 102.
  carbonate, in feed-water, 100, 221.
    removal of, from water, 176.
  chloride, in feed-water, 99, 221.
  formate, formation of, in boilers, 101.

Sodium hydroxide in feed-water, 221.
  nitrate, in feed-water, 222.
  sulphate, in feed-water, 222.
    electrolysis of, 22.
  sulphate, external deposits of, 90.
Softening plants, 179.
    continuous blow-down, 191.
    hot process, 190.
    irregular operation of, 93.
    permutit, 194.
  processes, 173.
Soft water, 82.
Soils, acidity of, 47.
  corrosivity of, 47.
Solution pressure, 19.
Soya bean oil, 159.
Spills, in condenser tubes, 113.
Spring water, 82.
Steam, action of, on iron, 46.
  supplies, subsidiary in condensers, 116.
Stimulating factors, summary of, 76.
Strain, effect of, on corrosion, 16, 37, 73
Stray currents, effect of, on corrosion, 34.
Structural heterogeneity, 71.
Structures, care in design, 134.
Sugars, formation of, in boilers, 102.
Sulphur, effect of, on corrosion, 66.
  in atmosphere, 55.
Sulphuretted hydrogen in water, 79.
Sulphuric acid, action of, on iron, 58.
    in water, 79.
Superheater troubles, 103.
  tubes, corrosion of, 46, 103.
Surface drainage water, 80.
  impurities, effect of, on corrosion, 70.
  wounds, 75.
Surrosion, 15.
Suspended matter in water, 82.

Temperature, effect of, on corrosion, 50, 61
Temporary hardness, 83.
    removal of, 173.
Tin coatings, 150.
  in condenser tubes, 114.
  effect of, on corrosion, 69.
Top inlet deterioration in condenser tubes, 116.
Tung oil, 159.
Tungsten, effect of, on corrosion, 70.
Turbines, corrosion in, 46, 104.
Turbulency, effect of, on corrosion, 49.
Types of corrosion, 34.

Ultramarine blue, pigment, 170.
Umber, pigment, 169.
Upland surface waters, 81.

Valency, 23.
Vanadium, effect of, on corrosion, 70.
Vapour deposition of zinc, 146.
Vegetable oils, 55.
Venetian red, pigment, 168.

Water, action of, on iron, 45.
  alkaline, 84.
  area of exposed surface of, 49.
  artesian well, 82.
  classification of, 79, 127.
  collection of impurities in, 79.
  colliery, 84.
  corrosive constituents in, 78, 87.
  deep-well, 82.
  dissolved gases in, 48, 198, 201
  for boiler-feed, 78.
  hard and soft, 82.
  peaty, 84.
  rain, 80.
    corrosivity of, 48.
  effect of rate of flow of, on corrosion, 48
  river, 81.
  scale-forming matter in, 78, 87.
  shallow-well, 80.
  speed in condensers, 117.
  spring, 82.
  stagnant, corrosion in, 49.
  surface drainage, 80.
  suspended matter in, 82.
  upland surface, 81.
Water-end, design in condensers, 119.
Well's process, 138.
White lead, pigment, 170.
Willow charcoal, pigment, 167.
Wounds, surface, 75.

Yellow, chrome, pigment, 168.

Zeolites, 83.
  artificial, 194.
Zinc barium chromate, pigment, 170.
  coatings, 143.
    processes of applying, 144.
    vapour deposition of, 146.
  chromate, pigment, 170.
  lead white, pigment, 171.
  oxide, pigment, 171.
  plating, 149.
  spraying, 150.
  yellow, pigment, 170.

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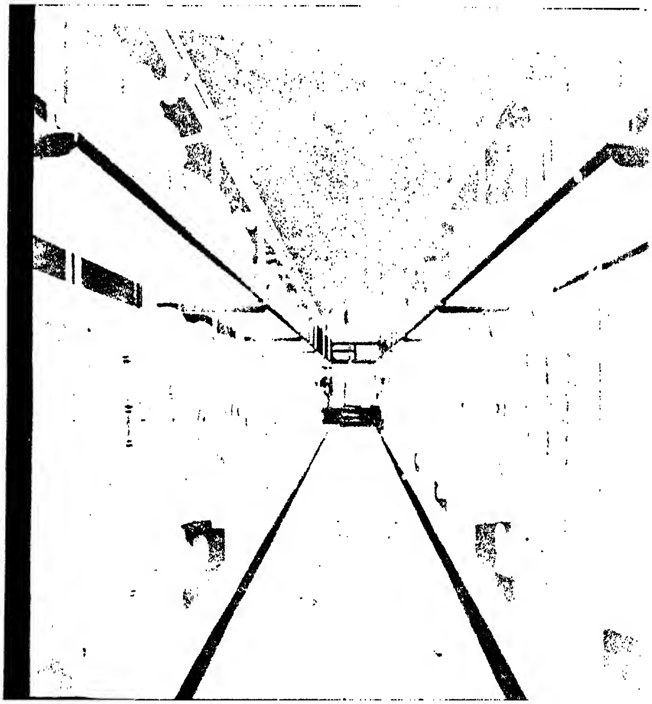

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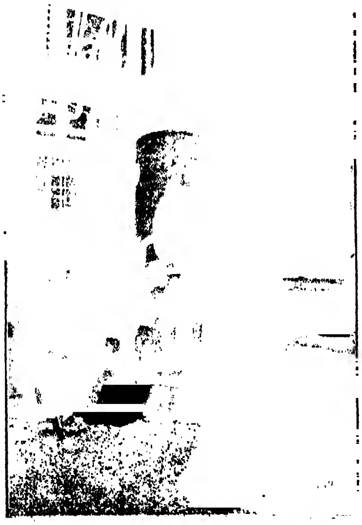

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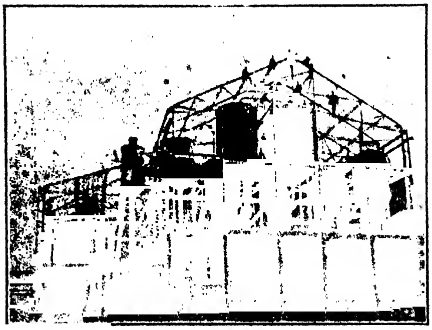

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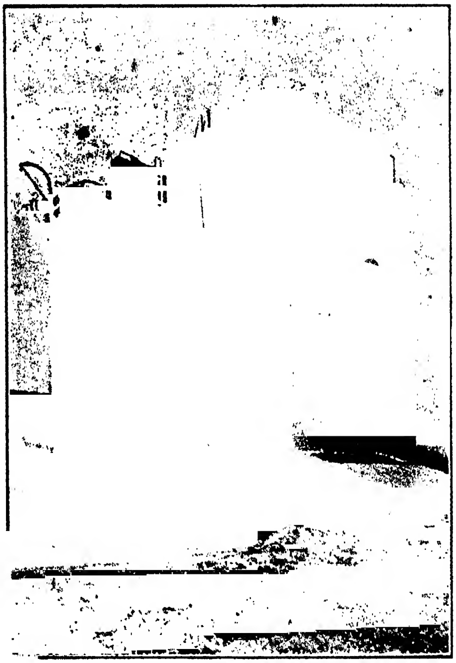

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